1968

Activated Carbon and Pyrolytic Decomposition Products From Cellulosics.

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ACTIVATED CARBON AND PYROLYTIC DECOMPOSITION PRODUCTS FROM CELLULOSICS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
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B.S., University of Delaware, 1961
M.S., Louisiana State University, 1966
January, 1968

ACKNOWLEDGMENT

This research project was carried out under the direction of Dr. Clayton D. Callihan, whose guidance and inspiration is gratefully acknowledged.

Appreciation is expressed to the Dow Chemical Company and to the National Aeronautics and Space Administration for their Fellowship support during the course of this work and to the Engineering Experiment Station for the use of experimental equipment. Appreciation is expressed to the South Coast Corporation for their financial support during many phases of this study.

Sincere thanks are due Mrs. Alma Oliver, Miss Hazel LaCoste, Mrs. Ruth Albright, and Mrs. Carol Houston, department secretaries for their assistance in procuring equipment and supplies and to Mr. L. M. Carpenter and Mr. Larry Veilleux for their aid in building equipment.

Grateful appreciation is also expressed to the Charles E. Coates Memorial Fund of the L.S.U. Foundation for paying the publication costs of this dissertation.

The author wishes to express his indebtedness to Mrs. Ruth Albright for her patience in typing this manuscript.

Without the enthusiastic encouragement and uncomplaining sacrifice of my wife, Susan, this undertaking would not have been possible.

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ABSTRACT

A new process for the production of activated carbon from cellulosics has been developed in which a portion of the number 2 and 3 carbon atoms of the anhydrous glucose units in the cellulose polymer chain are chemically oxidized to the aldehyde state using periodic acid. This results in cleavage of the ring structure at the bond between the vicinal diols which has the effect of increasing intramolecular mobility such that orientation of the carbon atoms into an active carbon lattice structure can occur with greater facility. The product from this treatment is carbonized at 450°C and then activated at 800-850°C using CO_2 as an activating medium. The chemical pretreatment results in a marked increase in the adsorptive capacity of the resulting chars as measured by their ability to adsorb methylene blue from water solutions. The adsorptive capacity of char made from cellulose without this chemical pretreatment was found to be 320 (mg. of methylene blue adsorbed/gm. of carbon). The adsorptive capacity was increased to 348 by cleavage of 2.3% and to 490 by cleavage of 9.9% of the 2,3 C-C bonds. Further increases in the cleavage treatment up to a level of 29.6% resulted in only a slight additional increase in the adsorptive capacity (to 500-515). The chars produced by this process have adsorptive capacities slightly better than those prepared by chemical treatment with zinc chloride before carbonization. The zinc chloride activation process probably proceeds by creating intermolecular mobility through cancellation of the Van der Waals forces between cellulose chains leading to partial solvation of the cellulose at elevated temperatures. Both the chars produced by an

increase in the intramolecular mobility (periodic acid treatment) and by an increase in the intermolecular mobility (zinc chloride treatment) showed an adsorptive capacity almost twice as high as any of the commercially available activated vegetable chars that were tested.

The decomposition products of cellulose during the carbonization reaction were also investigated. Batch pyrolysis without steam feed and continuous pyrolysis without steam feed were employed over a range of temperatures from 300 to 750°C. The yield of solid residue was found to increase by about 40% and the yield of noncondensable gaseous products was found to decrease by about 33% in going from batch to continuous pyrolysis at the same temperature with no steam feed. Batch pyrolysis with steam feed was also investigated.

In batch pyrolysis the rate of formation of condensable acid products in the vapor stream was enhanced by an acceleration of the heat-up rate and by a decrease in the partial pressure of steam. The total yield of acid products was relatively unaffected by these variables. The yield of noncondensable gaseous products was increased about three fold by the addition of steam to the reactor.

An increase in the temperature from 330 to 630°C for the continuous pyrolysis without steam feed produced a 380% increase in the yield of noncondensable gaseous products. The change in gas composition corresponding to this range of temperatures was: An increase from 28 to 45 mol % for CO, from 2 to 7 mol % for H_2, from 1 to 14 mol % for CH_4 and a decrease from 67 to 20 mol % for CO_2.

Gas chromatographic analysis of the condensed liquid overhead product from the continuous pyrolysis without steam feed indicated that the major components were water (about 85 wt. %) and acetic acid

(about 8 wt. %). The chromatograms indicated the presence of a large number of other compounds in small concentrations. Included among these were methanol, formic acid and formaldehyde.

CHAPTER I

INTRODUCTION

General Background

Manufacturing operations which utilize natural plants and trees as raw materials almost invariably have large amounts of residual materials that are primarily cellulosic in nature and for which there is little or no market. In the manufacture of sugar from cane this by-product is called bagasse. The Sugar Bulletin reports that in the state of Louisiana alone 2,200,904 tons of this material was produced in the 1966 grinding season (1). This quantity represents 31.6% of the 6,959,715 tons of cane ground. It is easy to see that a tremendous opportunity exists here for the utilization of ingenuity and technical knowledge in the pursuit of processes whereby these vast quantities of waste materials can be upgraded to useful products.

Effort has not been lacking. The technical literature is filled with various proposals for the utilization of these materials. Traditionally they have been used as sources of fuel but the heating value of bagasse on a dry basis is only 8000-9000 Btu/lb and the material as produced in the plant normally contains 40-50% water (2). The cellulosic wastes from other manufacturing operations would be expected to have an equally low heating value. In the last 50 years there has been a growing use of these materials to produce activated carbon (3). Other processes that have been reported include the manufacture of fiber board, paper pulp, ensilage, and carriers for molasses (4).

The Chemical Engineering Department at Louisiana State University has undertaken a multi-faceted attack under the direction of Dr. C. D. Callihan on the problem of finding new processes for the utilization of cellulosic waste materials. This report covers the initial investigations of thermal processes utilizing these materials. Other investigations underway include manufacture of ion exchange resins, biological manufacture of protein using cellulose as a substrate, and chemical treatment of cellulose to improve its digestibility for ruminant animals.

Thermal degradation of cellulose yields gaseous, liquid and solid products. The relative amounts of each of these products depends upon the starting material, the rate of heating, the final temperature, and the atmosphere maintained within the reactor (3, 4, 5, 6, 7). The gaseous products are primarily carbon dioxide and carbon monoxide with some methane and hydrogen also being produced. The liquid is predominantly water and lignin with a wide range of organic products being found in amounts from traces to about 3 wt. % of the cellulose fed. Schwenker and Beck (6) have reported that a minimum of 37 different volatile compounds are produced by the thermal degradation of cellulose. It is the solid residue made into activated carbon, however, that has yielded the most useful product in this research. Consequently, initial studies in this laboratory have concentrated on developing a new process for the production of an improved activated carbon from cellulosic materials.

In this research careful attention was paid to composition of both the gases and liquids coming off overhead, the liquid being condensed from the vapors. Rates of overhead compositions changes

were studied both as function of time and temperature. These compositions were being studied as a possible source of sythesis gas to be fed to a Fischer-Tropsch synthesis process. In this process carbon monoxide and hydrogen are passed over a catalyst at temperatures in the range of 200-500°C. A wide range of products including alkanes, alkenes and alcohols are produced. The type and amount of products are controlled by the type of catalyst and the temperature and pressure conditions in the reactor (8). The U.S. Department of the Interior, Bureau of Mines has done extensive research to develop this process in an attempt to increase the utilization of coal (9). They report that the process is nearing the point of being economically competitive.

Braunschweigische Maschinenbauanstalt in Germany has reported a process for the manufacture of furfural from agricultural by-products (10). They report a yield of furfural of 9% from bagasse. The investigation of this process and of similar processes will be pursued in future work by the Chemical Engineering Department's research group. The liquids condensed from the vapor phase of our process which were primarily composed of water and lignin, are being studied as possible sources of raw materials for other chemical processes. One such process which will be investigated in the near future is the catalytic dealkylation of lignin to produce phenol.

History of Activated Carbon

Mantell (3) gives an excellent summary of the historical development of decolorizing carbons. He reports that as early as the 15th century it was known that charcoal made by burning wood in a

closed vessel had the ability to remove coloring matter from solutions. This property was rediscovered by Lowitz in 1785 when he used it in the production of tartaric acid crystals. In 1794 wood charcoal was used in an English refinery for the clarification of raw sugar solutions. Since that time much effort has gone into the development of processes for the production of decolorizing carbons.

When the sugar industry began using bone char at the beginning of the 19th century the use of vegetable carbons and charcoal was almost eliminated. Their decolorizing power was slight when compared with bone char. However, early in the 20th century methods of activating these vegetable carbons were developed which increased their decolorizing power enormously, making them considerably more efficient than bone char. Carbons produced by these processes were termed activated carbons. Since that time their use in the sugar industry has been growing and, in addition, their use has been extended to include the purification of water through the elimination by adsorption of taste and odor producing impurities. Data from the U. S. Department of Commerce, Bureau of the Census (11) shown in Figure I-1 indicate a compounded annual growth rate of 6.8% in the total production of activated carbons. It is anticipated that this growth rate will accelerate as more emphasis is placed on the elimination of the pollution of our water resources.

Two forms of activated carbon are manufactured - powdered and granular. Granular carbons are almost always used in packed beds through which the liquid flows continuously. Powdered carbons are usually slurried into the liquid and later separated by filtration (12). Mantell (3) has divided the manufacturing methods for the production of

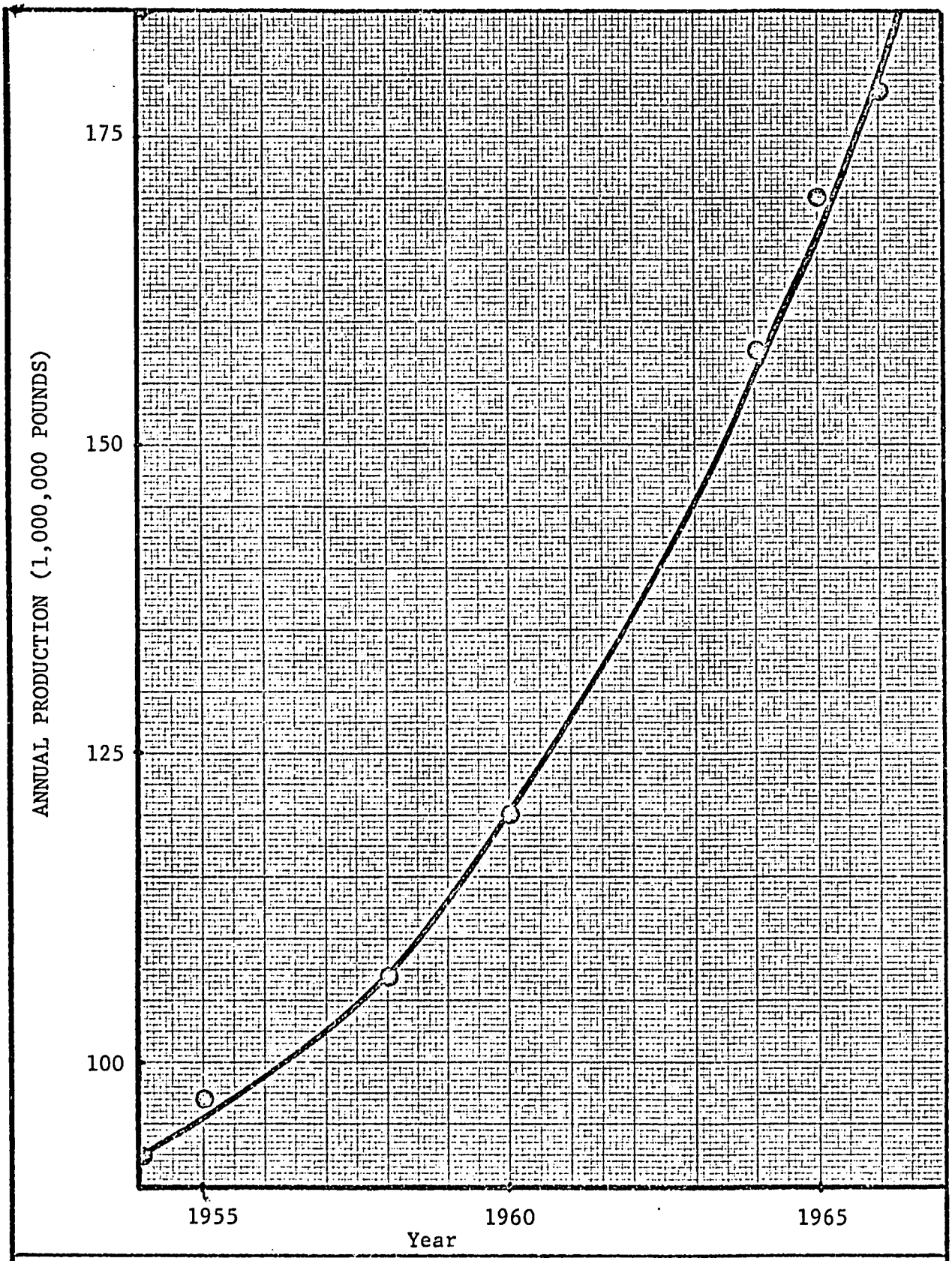

FIGURE I-1

RECORD OF TOTAL ANNUAL PRODUCTION OF ACTIVATED CARBON FOR ALL USES. DATA FROM U. S. DEPARTMENT OF COMMERCE, BUREAU OF THE CENSUS.

decolorizing carbons into three classes:

Class 1. Carbon is deposited as a layer on a porous inorganic base. The carbonized vegetable matter is mixed with porous substances such as infusorial earth, pumice stone or insoluble salts with or without the addition of a liquid binding medium. The mixture is heated to high temperatures resulting in the deposition of the carbon throughout the porous base. This gives a structure similar to bone char in which the carbon is dispersed throughout a structure of phosphorus salts.

Class 2. Carbon is deposited on inorganic bases which are afterwards spearated from the carbon by chemical treatment. In this process the vegetable matter is mixed with lime, chalk, sulfuric acid, calcium chloride, zinc chloride, magnesium chloride or phosphoric acid and then carbonized. Then the inorganic matter is dissolved out leaving the resulting carbon. The inorganic material serves as a dehydrating and an activating agent.

Class 3. Vegetable material is carbonized under controlled conditions of temperature and atmosphere. Activating temperatures are in the range of 800-900°C. Steam, air, carbon dioxide, or combinations of these gases are used as activating atmospheres.

Previous Studies

The literature is filled with conflicting data on the production of activated carbon from cellulosic materials. This was pointed out as early as 1922 by Coates (13) and has been reemphasized many times by other workers. This confusion is due to three factors: The lack of understanding of the mechanism of carbonization of cellulose under various pretreatment conditions, the lack of understanding

of the mechanism of activation, and the difficulty of obtaining a meaningful test of the degree of activation that could be easily reproduced by other workers.

In 1964 Tang and Bacon published an extensive study into the mechanism of carbonization of cellulose (5). They used infra red absorption spectroscopy and elemental analysis of chars to study cellulose fibers and films at various stages of thermal decomposition. Their results are summarized in Figure I-2 which is copied from Figure 5 pg. 218 of their article. It should be noted that they have departed from conventional notation in that the OH group on the number 3 carbon is normally shown within the ring. They state that this mechanism accounts only for the major reactions during the pyrolytic degradation of two cellulose units under conditions of a slow heating rate in an inert atmosphere. Consequently, it represents a considerably simplified picture of what actually occurs during degradation.

Stage I represents the physical desorption of water. This is a reversable process and the absorbed water can amount to as much as 12 weight percent.

Stage II is a dehydration step in which the equatorial hydroxyl and hydrogen moieties react through the formation of hydrogen bonded states. Under thermal excitation these moieties leave as water molecules. The proposition that this is an intramolecular rather than an intermolecular reaction is supported by the observation of the formation of ketone and olefin bonds.

Stage III represents the major portion of the thermal degradation. Temperatures above 240°C result in cleavage of C-O and C-C bonds resulting in the formation of large amounts of tar, water, CO

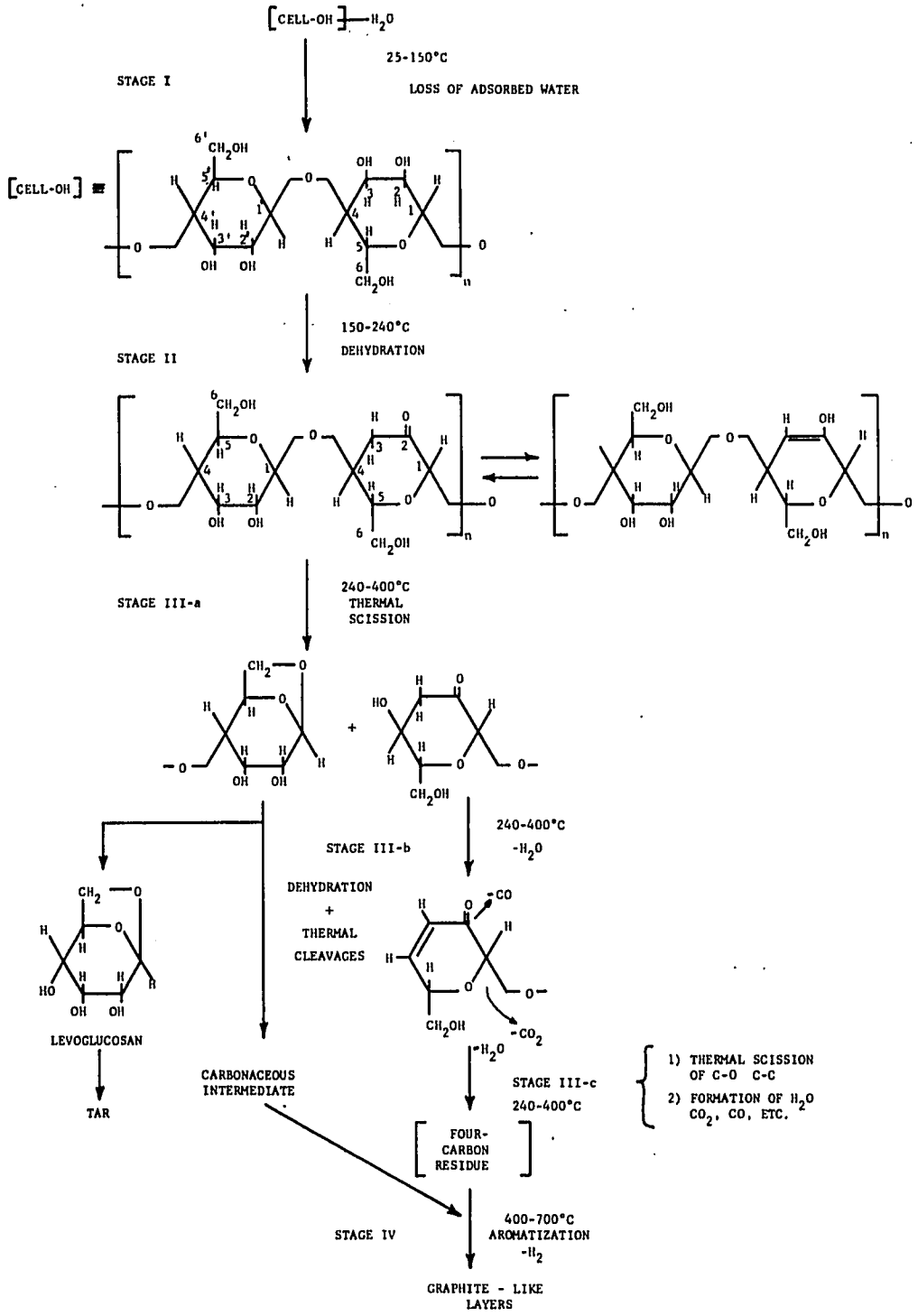

FIGURE I-2

PROPOSED MECHANISM OF TANG AND BACON FOR THE CONVERSION OF CELLULOSE TO CARBON. REFERENCE: CARBON, 2, pp 211-220 (1964).

and CO_2. The final breakdown of the cellulose units results in a four carbon residue which eventually repolymerizes into a "carbon polymer" which ultimately rearranges into a graphite structure. Tang and Bacon contend that this four carbon residue is made up of carbon atoms number 3, 4, 5 and 6 (refer to Figure I-2, the numbering system shown is standard). This is a most important point and it will be used later to develop the theory supporting a proposed new process for the manufacture of activated carbon.

In a subsequent paper (14) Tang and Bacon use X-ray diffraction data and fiber and film shrinkage data to establish that when these four-carbon residues polymerize, they do so predominantly along the axis of the original polymer chain rather than in a traverse direction across chains. These two possible modes of polymerization are shown in Figure I-3 which is taken from Figures 4 and 5 of their paper. It is obvious that this longitudinal polymerization requires that the four carbon residues reorient themselves before polymerization. Tang and Bacon state "It is to be emphasized that the proposed longitudinal polymerization process as illustrated schematically in Figure 4 (Figure I-3a in this report) is not meant to suggest any particular chemical mechanism of polymerization, but only to suggest that their exists a strong tendency to polymerize residues from cellulose ring units along the original cellulose chain direction prior to the formation of "cross links" to form graphite layers."

There have been many reasons proposed to account for the significant increase in the adsorptive power of carbons during the process of activation. Early investigators attributed this activation to removal of hydrocarbons from the pores in the carbon structure thereby

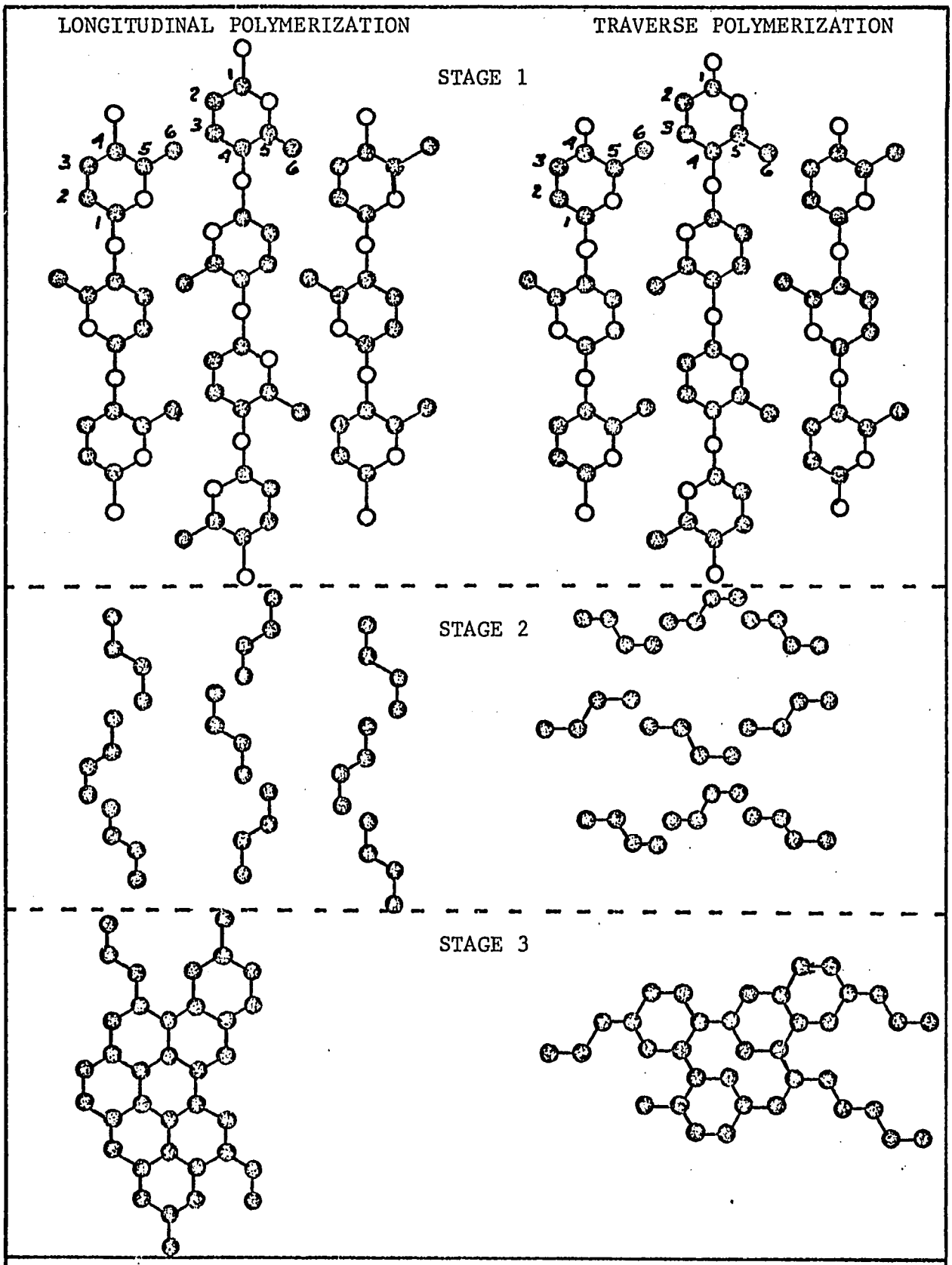

FIGURE I-3

GEOMETRY OF LONGITUDINAL AND TRAVERSE POLYMERIZATION PROCESSES FOR CONVERSION OF CELLULOSE RING UNITS INTO GRAPHITE LAYERS. REFERENCE: BACON AND TANG, CARBON, 2, 221-225 (1964).

increasing the surface area available for adsorption (15). This undoubtedly contributes to the activation but Lamont and Marsh (16) citing the evidence of Franklin (17), and Arnell and Barss (18) have shown that the major portion of the activation can be attributed to selective oxidation by the oxidizing medium (CO_2, steam, or air). They suggest that the internal porosity is blocked by short bridges or small regions of disordered carbon atoms which are considered to be more reactive than the hexagonal networks of the layer planes. The oxidizing atmosphere selectively removes these blockages and thereby makes the vast internal pore structure available for adsorption.

Proposed Process

Combining the results of Tang and Bacon (14) and Lamont and Marsh (16) one concludes that the production of activated carbon from cellulosic materials proceeds through the following steps:

1. Elimination of hydrogen, oxygen, and some carbon in a carbonization step that results in a residue consisting of the 3, 4, 5 and 6 carbons of the original cellulose molecule.

2. Longitudinal polymerization of this residue into a hexagonal graphite like carbon structure.

3. Preferential removal of straight chain carbon atoms linking the hexagonal structure.

Since it is the third step that leads to the large increase in the adsorptive power (activation) of the residue, a method of increasing the amount of straight chain carbon linkages was sought. The fact that only the 3, 4, 5 and 6 carbons remained after carbonization suggested that any treatment of the cellulose should involve these atoms. Also, the longitudinal polymerization theory suggested that something that could aid this polymerization mechanism could yield

significant advantages.

Periodic acid (HIO_4) is a very selective oxidizing agent that attacks vicinal diols to cleave the C-C bond and yield two aldehydes as shown in Figure I-4. Jackson (19) reports that if the hydroxyl groups are not attached to contiguous carbon atoms then no attack occurs. Jackson and Hudson (20,21) report that the reaction with cellulose and starch is quantitative and proceeds in 100% yield.

It was, therefore, proposed that the cellulose be pretreated by reacting a measured fraction of the vicinal diols with periodic acid before carbonization. This would increase the intramolecular mobility of the polymer chain and would place a portion of the number 3 carbons in the higher oxidized aldehyde state. On carbonization two possible reaction paths could then be followed. The oxidized number 3 carbons could decarbonylate before polymerization to the hexagonal structure or polymerization could occur without decarbonylation. In either case, the hexagonal structure would be broken up at the reacted number 3 carbon site. On activation these discontinuities in the carbon structure would be selectively attacked thereby opening up large amounts of internal surface area for adsorption.

As mentioned earlier, a major stumbling block in the study of activated carbons has been the method of testing the carbons for degree of activation. It was decided that adsorption of methylene blue from water solutions would be used as a criteria for degree of activation. This test has come into wide use in recent years and, consequently, would afford a means of comparison with previously reported results.

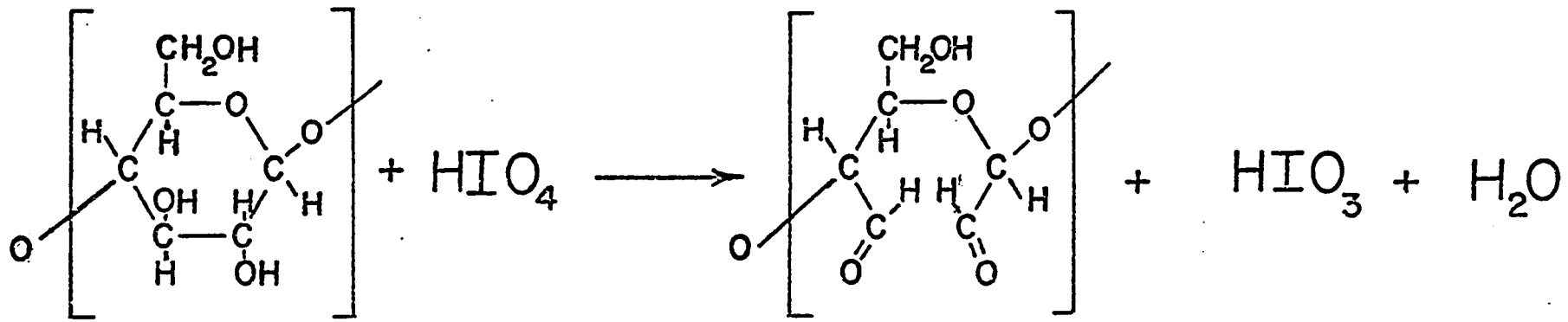

FIGURE I-4

PERIODIC ACID CLEAVAGE OF CELLULOSE RING

CHAPTER I

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CHAPTER II

EXPERIMENTAL APPARATUS AND PROCEDURES

Preparation of Bagasse Pith Feed

Feed material for these studies was bagasse pith from a 20 pound sample supplied by the Audubon Sugar Factory. This material was ground in a Wiley Mill Laboratory Grinder through 1/2mm or 1mm screens. The ground pith was then wet with an equal weight of water and pelletized in a laboratory pelletizer. The pellets were 1/8 inch in diameter and about 1/8 inch long. If the pith was not wet with the water before pelletizing the resulting pellets would not hold together and the pellet mill would usually plug up in a short time. The wet pellets were then dried overnight in a vacuum oven at 60-80°C and less than 2 inches of mercury absolute pressure. A slight air bleed was maintained through the oven during drying to sweep out the water vapor. The dried pellets were stored in closed containers until being fed to the reactor. If the pellets were stored wet they would ferment in about one week and would break apart. The dried pellets, however, could be stored for months with no apparent degradation.

Batch Pyrolysis Reaction Equipment

A flow diagram for the pyrolysis reactor is shown in Figure II-1. The reactor was 3/4 inch I.D. monel tubing 43 inches long. A 1/4 inch O.D. 316 stainless steel thermowell passed through a 3/4 inch monel pipe tee on the bottom of the reactor and extended to a height of 42 inches within the reactor. Into this thermowell a thermocouple assembly consisting of eight chromel-alumel thermocouples spaced

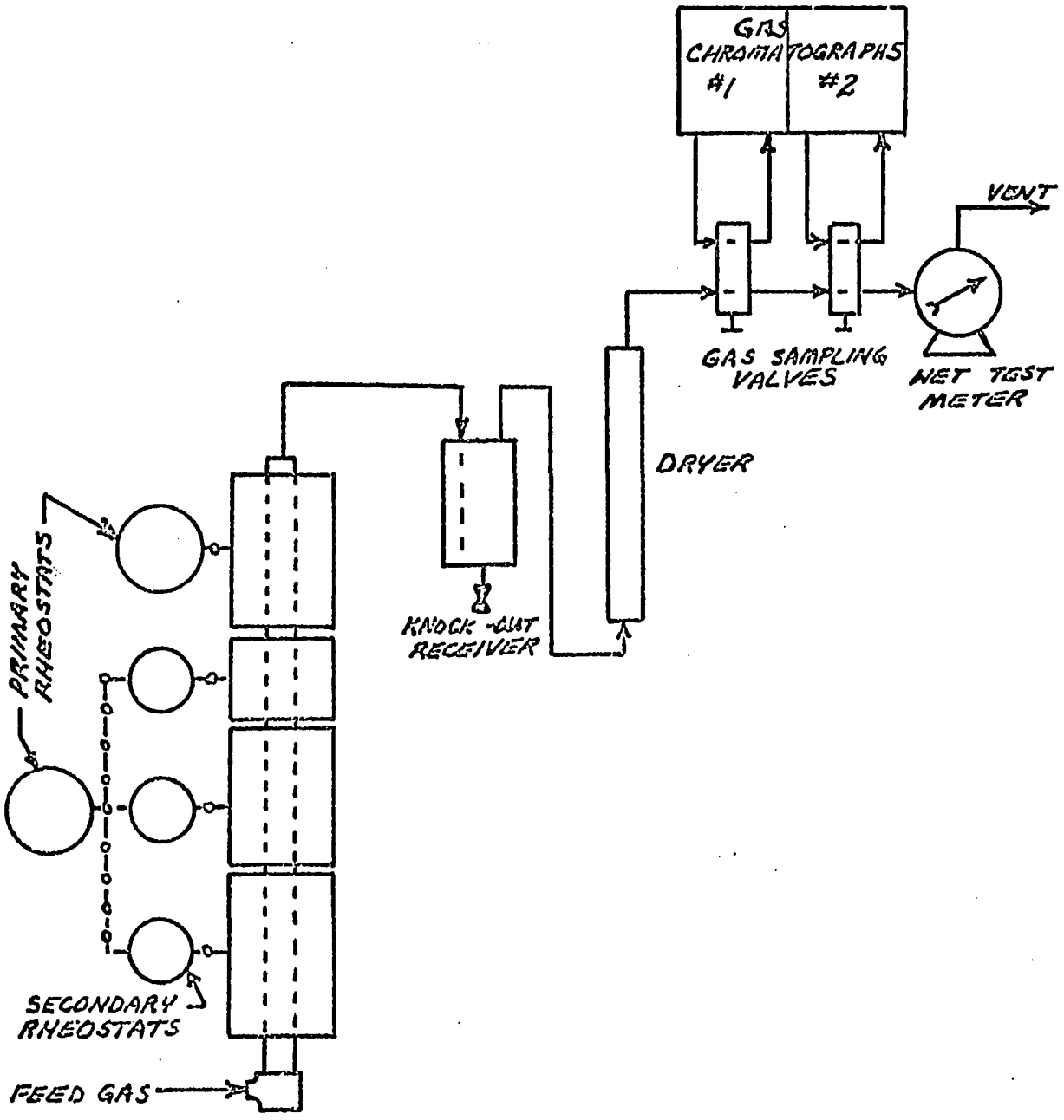

FIGURE II-1

REACTOR FLOW DIAGRAM FOR BATCH REACTION EXPERIMENTS

W.R. Williamson
August 31, 1967

4 inches apart was inserted. The maximum height to which this assembly could be inserted into the thermowell was about 36 inches. The thermocouple outputs were recorded on a multipoint temperature recorder with a range of 0-1000°C.

Heat was provided for the reactor by four combustion furnace sections capable of achieving temperatures of up to 1000°C. The lengths of these sections were No. 1 (top) = 12 inches; No. 2 = 4 inches; No. 3 = 8 inches; No. 4 (bottom) = 12 inches. Sections 2, 3, and 4 were split and hinged, section 1 was not split. One inch of insulation separated each heating element (1/2 inch on the end of each element). This brought the overall heated length counting the insulation sections to 40 inches. Approximately 3 inches of the reactor plus the monel tee extended below the bottom heater. The top of the reactor was fitted with a 3/4 x 1/4 inch monel reducer that had been machined down so that it would fit inside the top heater section. In operation, the top of this reducer was maintained level with the top of the upper heater.

The voltage across the No. 1 heater was adjusted by a heavy duty primary rheostat. The voltage to the other three heaters was adjusted by individual secondary rheostats the three of which were in turn all connected to a large capacity primary rheostat. The primary rheostats were used to attain the desired temperature level and the secondary rheostats were used to make adjustments in the temperature distribution.

Since heat losses from the bottom of the reactor were quite high, a piece of 3/8 inch I.D. steel pipe 10 inches long was placed into the bottom of the reactor. About one inch of glass wool

insulation was placed on top of this pipe to prevent the feed material from dropping below this level. The reactor was never filled to a level greater than 2 inches below the top. About 1 inch of glass wool was packed into the reducer at the top to prevent the entrainment of any solid material in the vapors leaving the reactor.

Steam was fed into the branch of the tee at the bottom of the reactor. It was supplied by pumping water with a laboratory bellows pump through a 1/4 inch O.D. copper coil 3 feet long that was inserted into a combustion furnace heater. The steam generated in this heater passed through 1/4 inch copper tubing that was wrapped with heating tape covered with two layers of asbestos insulation. A flow diagram of this system is shown in Figure II-2. In order to maintain a constant water feed rate through the bellows pump it was necessary to maintain a constant pressure at the pump inlet. This was achieved by using the constant head device shown in Figure II-3. The principle of operation of this device is as follows (refer to Figure II-3):

1. The tank and vent line are filled with water and the pump is started.

2. The level in the vent line will drop until it is completely empty. At that point the pressure at level A must be one atmosphere since the vent line is free of any liquid.

3. As the pump continues to pump liquid from the tank, the liquid level will drop and air will enter through the vent line.

4. The pressure at level A will remain constant at one atmosphere no matter what the liquid level in the tank. Consequently the inlet pressure for the pump will remain constant as long as the liquid level in the tank is higher than level A.

This device worked very well allowing constant water feed at

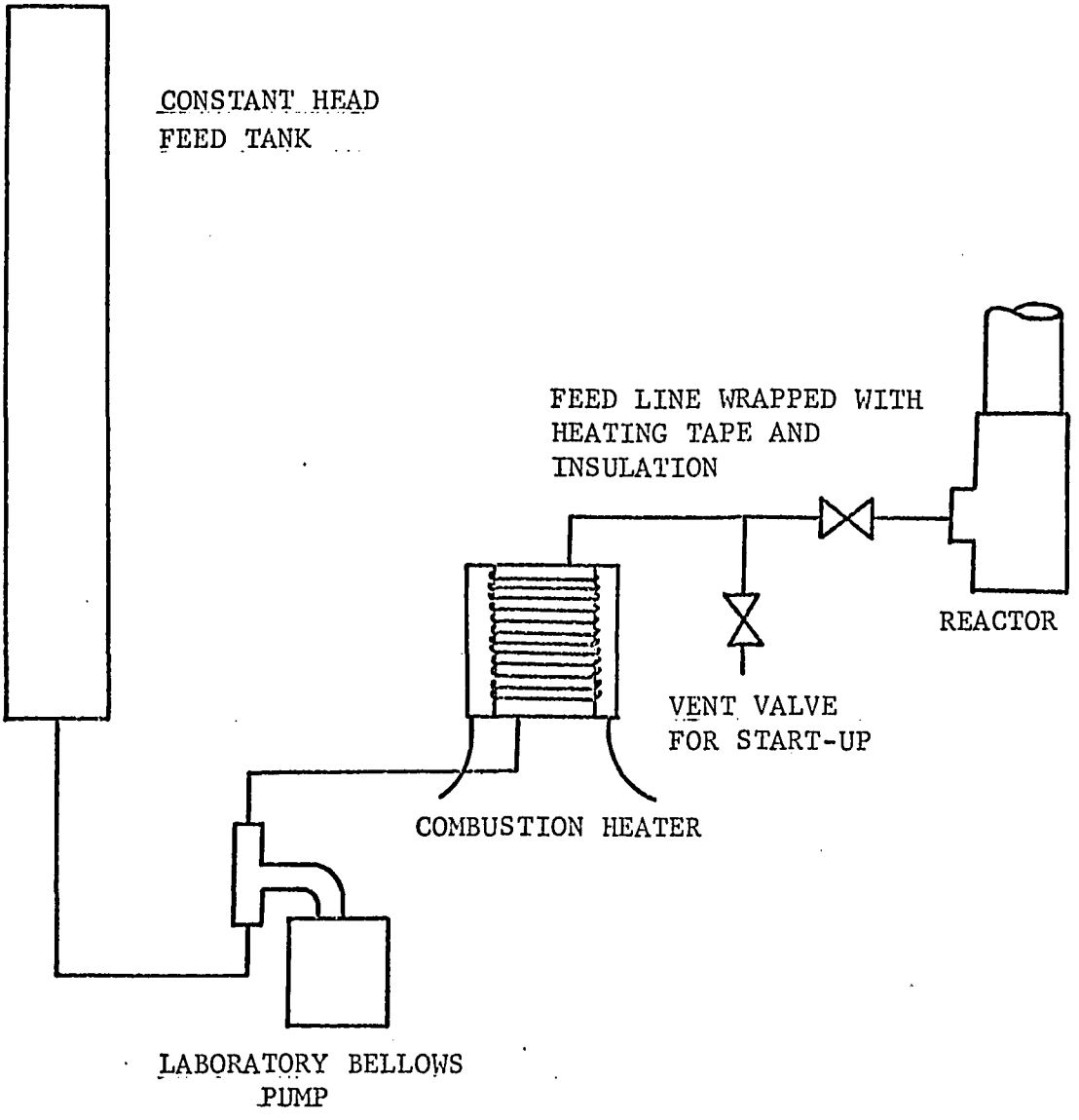

FIGURE II-2
FLOW DIAGRAM FOR STEAM GENERATING APPARATUS
DRAWN BY: W. R. Williamson
DATE: September 13, 1967

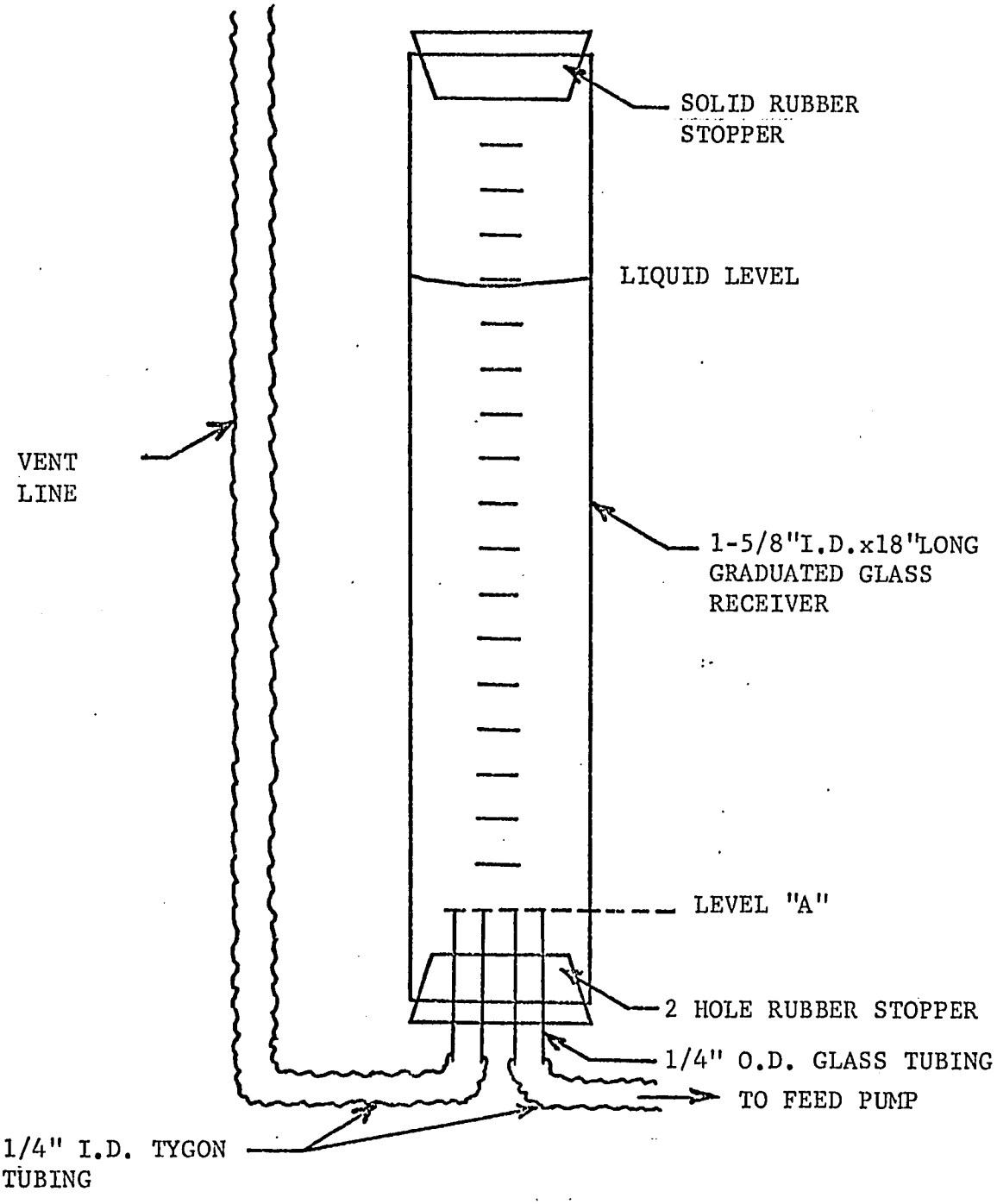

FIGURE II-3

CONSTANT HEAD FEED TANK

DRAWN BY: W. R. Williamson

DATE: September 13, 1967

rates as low as 0.1 cc/min.

Overhead vapors from the reactor passed through 1/4 inch O.D. type 316 stainless steel tubing wrapped with heating tape and asbestos insulation into a knock-out receiver made from 4 inch O.D. glass pipe 1 foot long. Gas from this receiver flowed through a 1/4 inch O.D. cooling coil (straight length of 6 feet) that was immersed in an ice-water bath. The outlet from this coil flowed into another knock-out receiver then through a 1 inch I.D. by 3 feet long drier packed with calcium sulfate dessicant. Effluent from this drier flowed through two gas sampling valves then through a wet test meter and was vented out of the window.

Batch Pyrolysis Reaction Procedure

The pelletized feed material was weighed into the reactor (60-90 grams per charge) and the reactor was placed into the heaters. The heaters were turned on and the reactor was heated to the desired temperature. Steam feed was started when the reactor temperature reached 110°C. Temperature readings, overhead liquid samples, gas samples, and wet test meter readings were recorded periodically. Gas samples were analized by gas chromatography for CO, CH_4, CO_2, and H_2. After reacting for the desired amount of time the heaters were turned off and the reactor was allowed to cool slowly to room temperature. The residue was then removed and weighed and the reactor was cleaned by pushing a cloth through it several times. It was sometimes found necessary to heat the bottom flange and the sampling valve of the first knock-out receiver in order to keep the liquid samples at a sufficiently low viscosity to allow them to flow out in a short period of time (30 seconds).

Continuous Pyrolysis Reaction Equipment

The equipment used in the continuous reaction studies was basically the same as that used in the batch reaction studies but the reactor was modified so that it could be fed continuously. A solids feed valve (Figure II-4) was built in the Chemical Engineering Department shop. This valve consists of a rotating brass cylinder fitted into a brass body. Four slots about 3/4 inch long by 1/4 inch wide by 1/2 inch deep were cut into the cylinder 90° apart. Two 3/4 inch I.D. pipe nipples 2 inches long were brazed to the valve body 180° apart and perpindicular to the axis of the valve body. In operations the solid feed material flowed by gravity from a feed reservoir (Figure II-5) into the top pipe nipple. As the cylinder rotated, one of the slots would be filled with feed material as it passed the top nipple. This slot would then empty its contents into the bottom nipple from which the material would flow by gravity into the reactor. The valve was turned by a chart drive motor removed from a recorder. This motor developed a torque at 1800 rpm of 45 inch ounces. Gear reducers were used to provide a rotational speed of 1.5 rpm for the valve cylinder. Provisions were made for increasing or decreasing this speed by a factor of 2 by the change of one set of easily accessible gears.

The feed reservoir (Figure II-5) was a 1-1/2 inch glass pipe 3 feet long with flanges on each end. A 1 rpm clock motor was mounted on the top flange to turn a 1/8 inch diameter brass agitator that was used to prevent bridging of the feed in the reservoir. The feed reservoir and the feed valve were wrapped with heating tape and asbestos insulation.

The reducer that was used at the top of the reactor in the

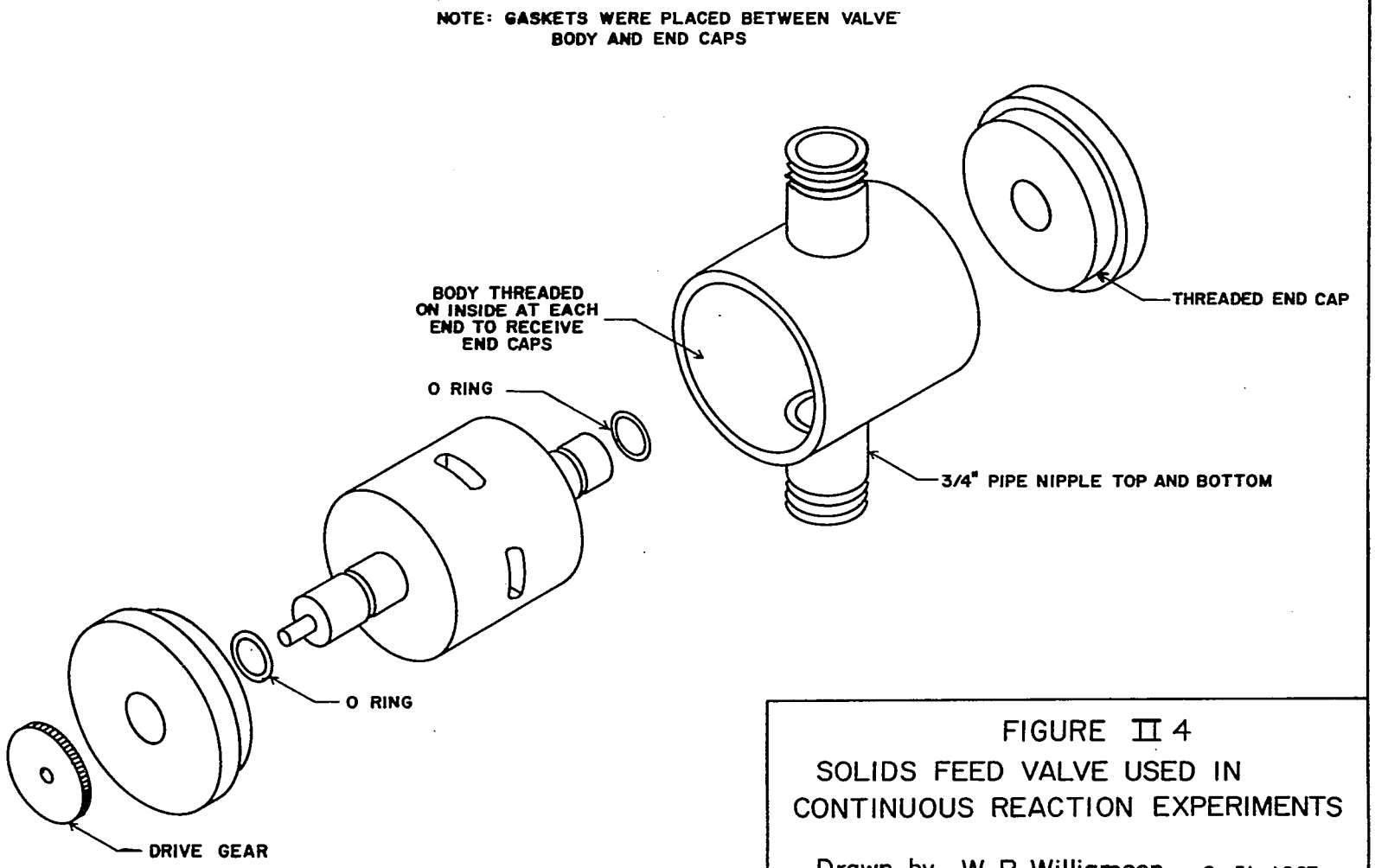

FIGURE II 4

SOLIDS FEED VALVE USED IN CONTINUOUS REACTION EXPERIMENTS

Drawn by- W. R. Williamson 8-31-1967

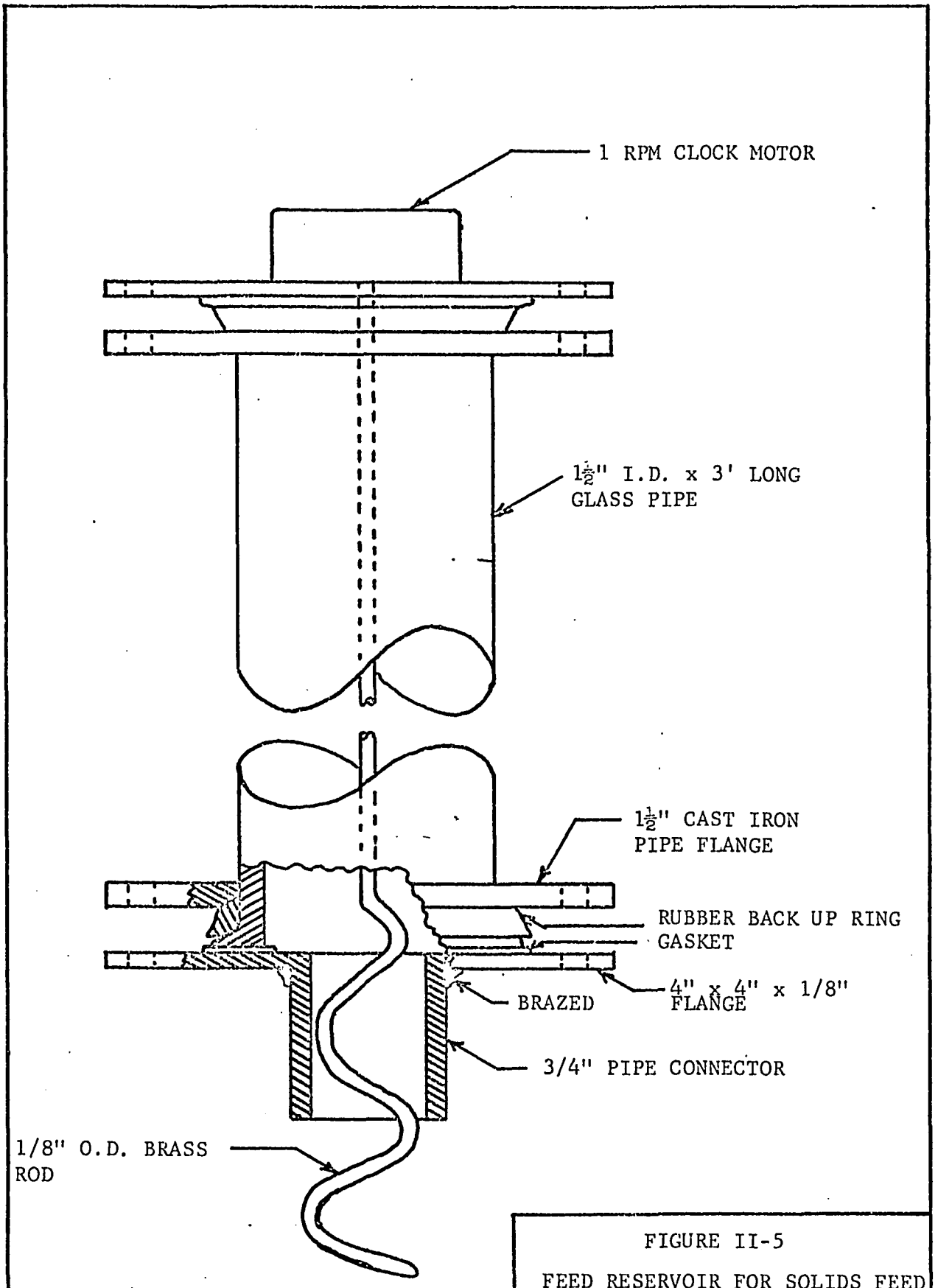

FIGURE II-5

FEED RESERVOIR FOR SOLIDS FEED VALUE

W. R. Williamson Sept. 27,1967

batch reaction studies was replaced with a 3/4 inch monel pipe tee. The feed valve was attached to the run of this tee so that the feed material would drop straight through the tee. The vapors leaving the reactor exited through the branch of the tee and entered the same recovery train used in the batch reaction studies. A Syntron® laboratory vibrator was attached to the tee at the top of the reactor and another was attached to the tee at the bottom. A photograph of the complete feed assembly is shown in Figure II-6.

Continuous Pyrolysis Reaction Procedure

The feed reservoir was filled with the pelletized pith (about 100 grams) and the reservoir and feed valve were attached to the reactor. The reactor was brought up to temperature and the valve and reservoir were heated to about 110°C with the heating tapes. The feed valve and the reservoir agitator were started and the vibrators were turned on. Feed entered the reactor at an average rate of about 0.7 grams per minute.

It was found that if the feed valve and reservoir were not heated to above 100°C the vapors coming from the initial feed would condense moisture on the pellets being fed. As soon as these pellets came into contact with liquid water they would swell. The pellet would break up into an indiscriminate mass that immediately clogged the valve and the top of the reactor preventing any additional feed from entering the reactor. As long as the water vapor was prevented from condensing by preheating the feed, no problems of this type were encountered.

If the vibrators were not used, the feed material had a tendency to bridge in the reactor particularly at the top of the

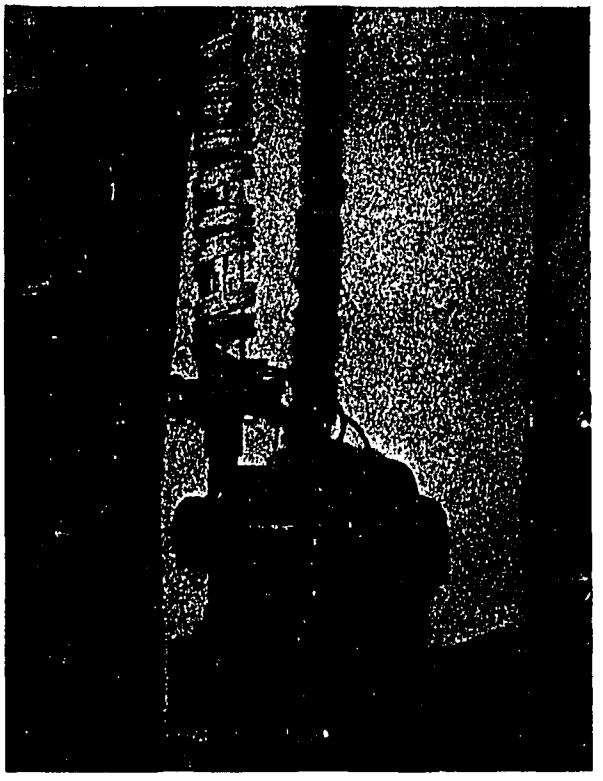

FIGURE II-6

PHOTOGRAPH OF CONTINUOUS FEED ASSEMBLY. INSULATION HAS BEEN REMOVED FROM FEED RESERVOIR TO SHOW INTERNALS.

thermowell. Using the two vibrators minimized this problem but it was still encountered on some of the high temperature runs.

Periodic Acid Cleavage Reaction

The feed material used in these studies was a high purity filter paper (Whatman No. 2). The periodic acid was Reagent Grade $HIO_4 \cdot 2H_2O$ manufactured by the G. Frederick Smith Chemical Company of Columbus, Ohio.

The filter paper was cut into squares about 1/2" on a side. About 100-300 grams of this material was weighed into a three liter resin kettle. About 2.5 liters of 0.15-0.60 M periodic acid solution was poured into the kettle making a thick slurry. The mixture was stirred with an air driven agitator. Samples of the reaction liquid were removed and tested for periodic acid concentration. The analytical procedure is given on page 34.

When the reaction had progressed to the desired extent, the reaction mixture was filtered. The filtrate was saved to be used in subsequent runs. The filter cake was washed repeatedly with water (up to 10 liters of water used to wash some samples). After the final wash, the filter cake was dried in the vacuum oven at 80°C and 1 in. of Hg. abs. pressure overnight. A slight air bleed was introduced into the vacuum oven during drying to facilitate water removal. It was observed that the filter cake had an odor characteristic of periodic acid even after extensive washing. Also, during drying the filter cake turned brown indicating that all of the periodic acid had not been removed. This color change was most pronounced at the top of the

filter cake in the drying pan.

Pyrolysis of Cleavage Reaction Product

The dried material was carbonized in a vented bomb made from a 4 inch steel pipe nipple 6 inches long. One end of this nipple was sealed with a piece of 1/8 inch steel plate welded to the nipple. The other end of the nipple was fitted with a 4 x 2-1/2 inch bell reducer into which was screwed a 2-1/2 inch pipe plug. This plug was drilled through and tapped for a 1/4 inch pipe to tubing adapter. A short piece of copper tubing was fitted to this adapter to provide a vent for the bomb.

Material to be carbonized was weighed into the bomb (150-180 gm. per charge) and the bomb was placed in a muffle furnace at 400-500°C. Copper tubing was connected to the short piece of copper tubing attached to the bomb to provide a vent out of the reactor room window. The bomb was left in the muffle furnace for 24-48 hours then taken from the oven and cooled. The bell reducer was removed and the carbonized material was weighed.

On cooling, the short piece of copper tubing attached to the bomb was found to be plugged with a carbonatious material (usually less than one gram).. This piece of tubing was, consequently, replaced after each run.

Activiation Reaction Equipment

The equipment used to activate the residues was the same as that used in the batch reaction studies described previously. The tee at the bottom of the reactor was replaced with a 3/4 inch type 304 stainless steel pipe cross. Provisions were made to feed carbon dioxide into one of the branches and steam into the other branch of this

cross. The thermowell was inserted through the run of the cross as it had been through the run of the tee before.

Activation Reaction Procedure

The carbonized products were fed to the reactor batchwise and the reactor was inserted into the heaters. Carbon dioxide was fed through a rotometer at a rate of 0.0065 ft^3/min. The heaters were turned on and the reactor was brought up to a temperature of 800-850°C. About two hours were required to reach this temperature. A typical record of the average reaction temperature during start up is given in Figure II-7. Gas samples were taken periodically and the temperature and wet test meter readings were recorded. At the end of the run the heaters and the carbon dioxide flow were turned off and the reactor was cooled to room temperature. A period of about three hours was required for the reactor to cool sufficiently to be handled but frequently it was allowed to cool overnight. After cooling the reactor was opened and the residue was weighed. The cross at the bottom of the reactor was removed to insure that there was no holdup of residue in the reactor.

Analysis of Overhead Gas

The overhead gas stream was made up of carbon dioxide, carbon monoxide, hydrogen and methane and was analyzed by means of gas chromatography. It was found that if helium was used as a carrier gas the response to hydrogen was very low while if argon was used as the carrier gas the response for all components except hydrogen was very low. The results confirm those of Madison (1) who reports a minimum in the thermal conductivity curve for hydrogen-helium mixtures. Consequently, two gas chromatographs were used with helium being used as

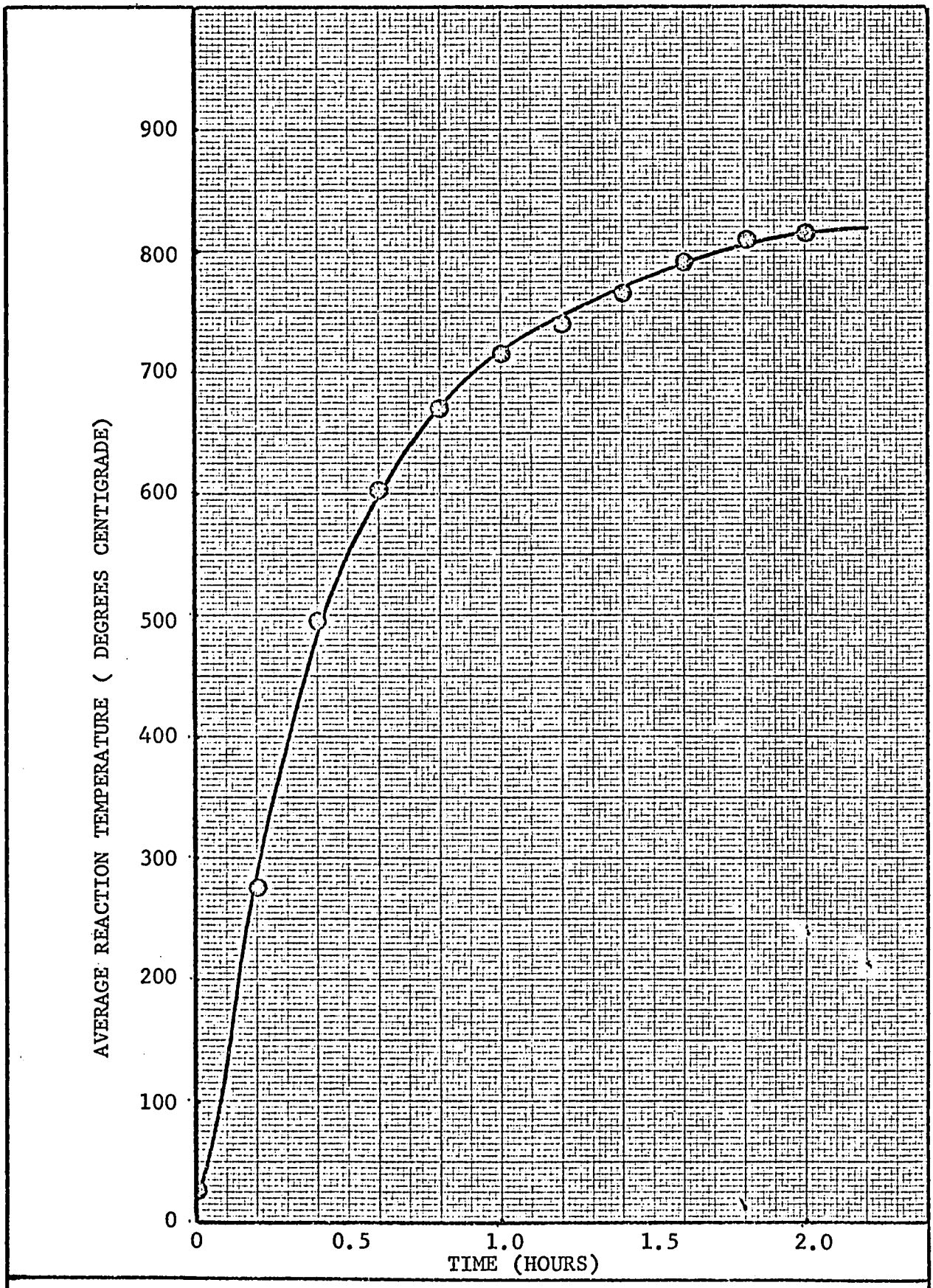

FIGURE II-7
TYPICAL RECORD OF AVERAGE REACTOR TEMPERATURE DURING START-UP PERIOD OF ACTIVATION REACTION.

carrier gas in one and argon being used as carrier gas in the other. A gas sampling valve was provided for each chromatograph (one being purchased from Microteck Corp., Baton Rouge, Louisiana the other being made in the Chemical Engineering Department Shop). Each of these valves had a sample loop of about 1 cc capacity.

Since the gas sampling valves always introduced exactly the same size sample into the chromatograph each time a sample was taken, it was possible to use peak height on the resulting chromatogram as a measure of component concentration. The response of the chromatograph is actually a measure of the amount of material flowing over the detector. This fact plus the constant volume of the sample loop made it possible to calibrate the chromatograph using reduced pressure pure gas samples rather than gas mixtures. The sample loop was filled with a sample of the pure gas at a slight positive pressure. Then the pressure was carefully reduced by means of a vacuum pump to some desired value. This reduced pressure sample was then introduced into the carrier gas stream and the peak height response on the chromatograph was measured. The mole fraction of a mixed gas sample which would give this same peak height response was calculated using the equation:

$$f = \frac{p}{P}$$

where f = mole fraction

p = pressure of gas sample (inches of Hg absolute)

P = atmospheric pressure (inches of Hg absolute)

The calibration curves obtained using this technique are given in Figure II-8. Using this technique the gas analysis usually summed to 95-105 mol % and no normalization of the results was

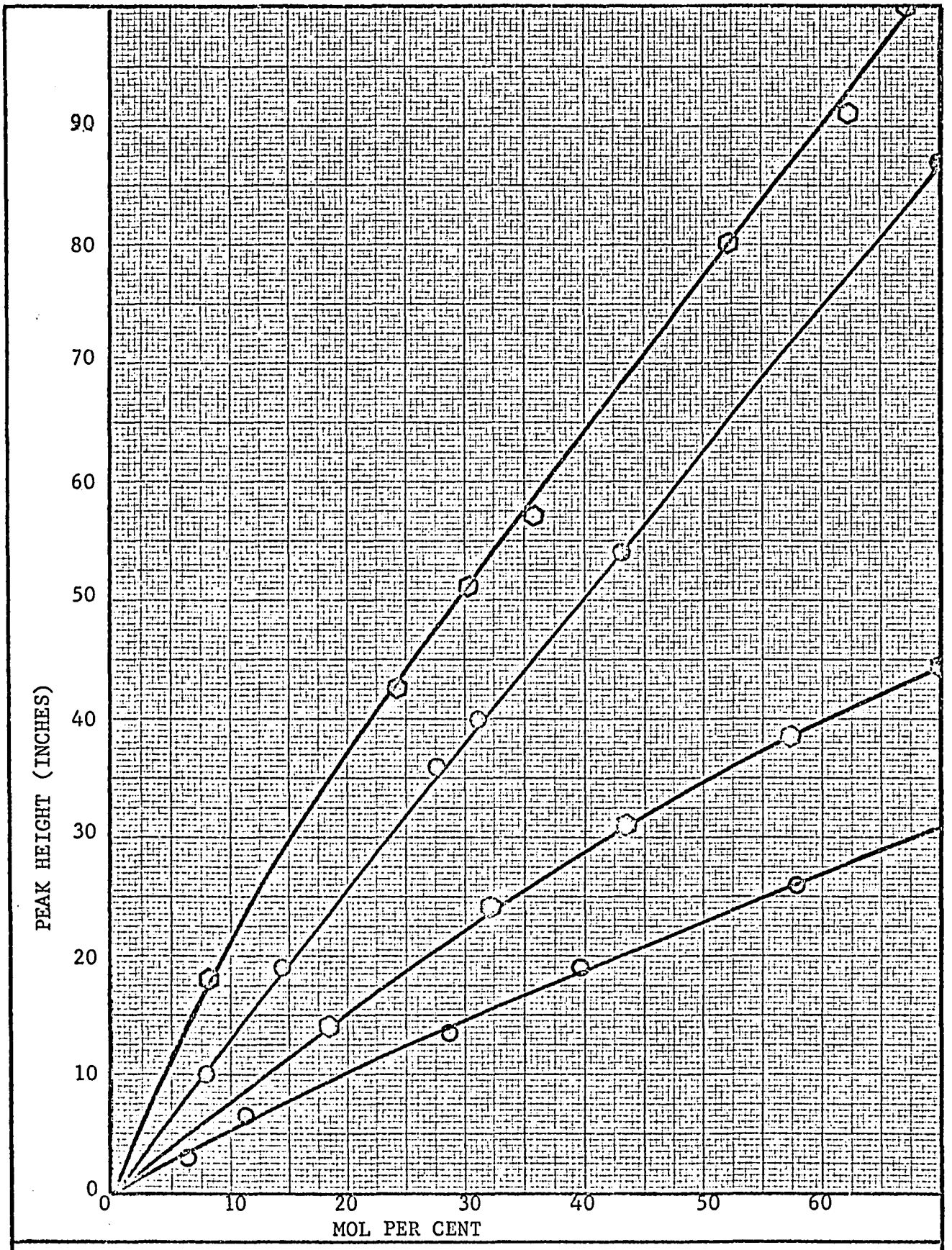

FIGURE II-8
TYPICAL CALIBRATION CURVES FOR GAS CHROMATOGRAPH. DATA ON CHROMATOGRAPH CONDITIONS ARE GIVEN ON NOTEBOOK REFERENCE 1-105.

necessary. The chromatograph conditions used in this work are given in Table II-1.

Analysis of Overhead Liquid

Analysis of the overhead liquid was done on a Micro Tek GC 2500 R Gas chromatograph. The column temperature was programed in the following sequence:

Initial Temperature 90°C for 2 minutes
Program Temperature Increase of 10°C/min for 10 minutes
Final Temperature of 230°C Held for 9 minutes

The column used was 1/4 inch I.D. by 8 feet long Porapak Q column supplied by Waters Associates of Framingham, Massachusetts. Carrier gas was helium at a rate of 40 cc/min.

Analysis of Periodic Acid Solution

The method of Fleury and Lange (2) as described by Jackson (3) was used for analysis of the periodic acid solution and is outlined below. The method of preparing and testing the iodine solution is that of Rieman, Neuss, and Naiman (4).

I. Reagents Required

A - 0.1 N sodium arsonite solution
B - 0.1 N iodine solution
C - 0.1 N arsenious oxide (primary standard)
D - 20 wt. % potassium iodide solution
E - sodium bicarbonate powder
F - starch indicator

II. Apparatus Required

A - 10 cc buret
B - 50 cc buret
C - 250 ml erlenmeyer flask

TABLE II-1. Gas Chromatograph Operating Conditions

A - Hydrogen Analysis

Chromatograph - Fisher - Gulf Partitioner

Column

1/4 inch I.D. x 5 feet long Columnpak (C)* (60-80 mesh)

1/4 inch I.D. x 7 feet long Molecular Sieve 13X(42-60 mesh)

Temperature - Room Temperature

Carrier Gas - Argon

Carrier Gas Flow = 37.7cc/min.

B - Carbon Monoxide, Carbon Dioxide and Methane Analysis

Chromatograph - Consolidated Electrodynamics Corp. Type 26-201A

Column

1/4 inch I.D. x 7 feet 10 inches long Porapak (C)Q** (50-80 mesh)

Temperature - Room Temperature

Carrier Gas - Helium

Carrier Gas flow = 37.7 cc/min.

* Obtained from Fisher Scientific Company, 690 Miami Circle, N.E. Atlanta, Georgia, 30324.

**Obtained from Waters Associates, 61 Fountain Street, Framingham, Massachusetts, 01701.

III. Reaction

$$AsO_2^- + HIO_4 \longrightarrow HIO_3 + AsO_3^-$$

$$AsO_2^- + I_2 + 2H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2I^-$$

IV. Procedure

The sample of periodic acid solution (5cc for approximately 0.2m or 2cc for 0.5m solution) is diluted to 10cc with distilled water. This solution is neutralized with about 1.5 gm of $NaHCO_3$ then an excess (25-30cc) of 0.1N sodium arsenite solution and 1cc of a 20 wt % potassium iodide are added. After standing for 10 to 15 minutes, 2 cc of starch indicator is added and the mixture is titrated with 0.1N iodine solution until the appearance of a faint blue color.

V. Calculations

The molarity of the periodic acid sample is calculated as follows:

$$\text{G.E.W. of As added} = N_{NaAsO_2} \quad v_{NaAsO_2}$$

$$\text{G.E.W. of I added} = \underline{N_I \quad v_I}$$

$$\text{G.E.W. of } HIO_4 = \text{(Difference)}$$

$$M_{HIO_4} = \frac{\text{(Difference)}}{(2)(\text{vol. sample})}$$

Example

sample = 2cc

$NaAsO_2$ solution added = 25cc of 0.1054N solution

Iodine solution used = 7.10cc of 0.1097N solution

G.E.W. of $NaAsO_2$ = (0.025)(0.1054) = 0.002635

G.E.W. of Iodine = (0.00710)(0.1097) = 0.000779

G.E.W. of HIO_4 in sample 0.001856

$$M = \frac{0.001856}{(2)(0.002)} = 0.464$$

Analysis for Degree of Activation of Carbon

Samples of the carbon being tested were weighed to ± 0.0001 gm into 29mm I.D. by 105mm long (volume capacity of 50cc) polypropylene centrifuge tubes. From four to sixteen samples of each carbon covering a range of weights from 0.5000 to 0.0400 grams were used. Thirty-five cc of a standard methylene blue solution (concentration equal to 2480 ppm) from a 6.5 gallon carbouy was added to each tube by means of a 50cc automatic zeroing buret and the tubes were stoppered with a number 5 1/2 rubber stopper. Thus the carbon dosages, M, ranged from 0.0142 to 0.00114 grams of carbon per gram of solution. The tubes were shaken vigorously by hand and let stand for 48 hours with occasional shaking. The samples were centrifuged for five minutes and a 2cc portion was removed with a pipette and diluted to a concentration of less than 30 ppm.

The concentration of methylene blue was determined colormetrically using a Beckman Model B spectrophotometer. Absorbance relative to distilled water was measured at a wavelength of 620 mμ using a sample length of 10mm. A calibration curve of absorbance vrs. methylene blue concentration was made and is shown in Figure II-9. The actual concentration of methylene blue in the original sample was determined using the dilution factor and the change in concentration, X, was calculated.

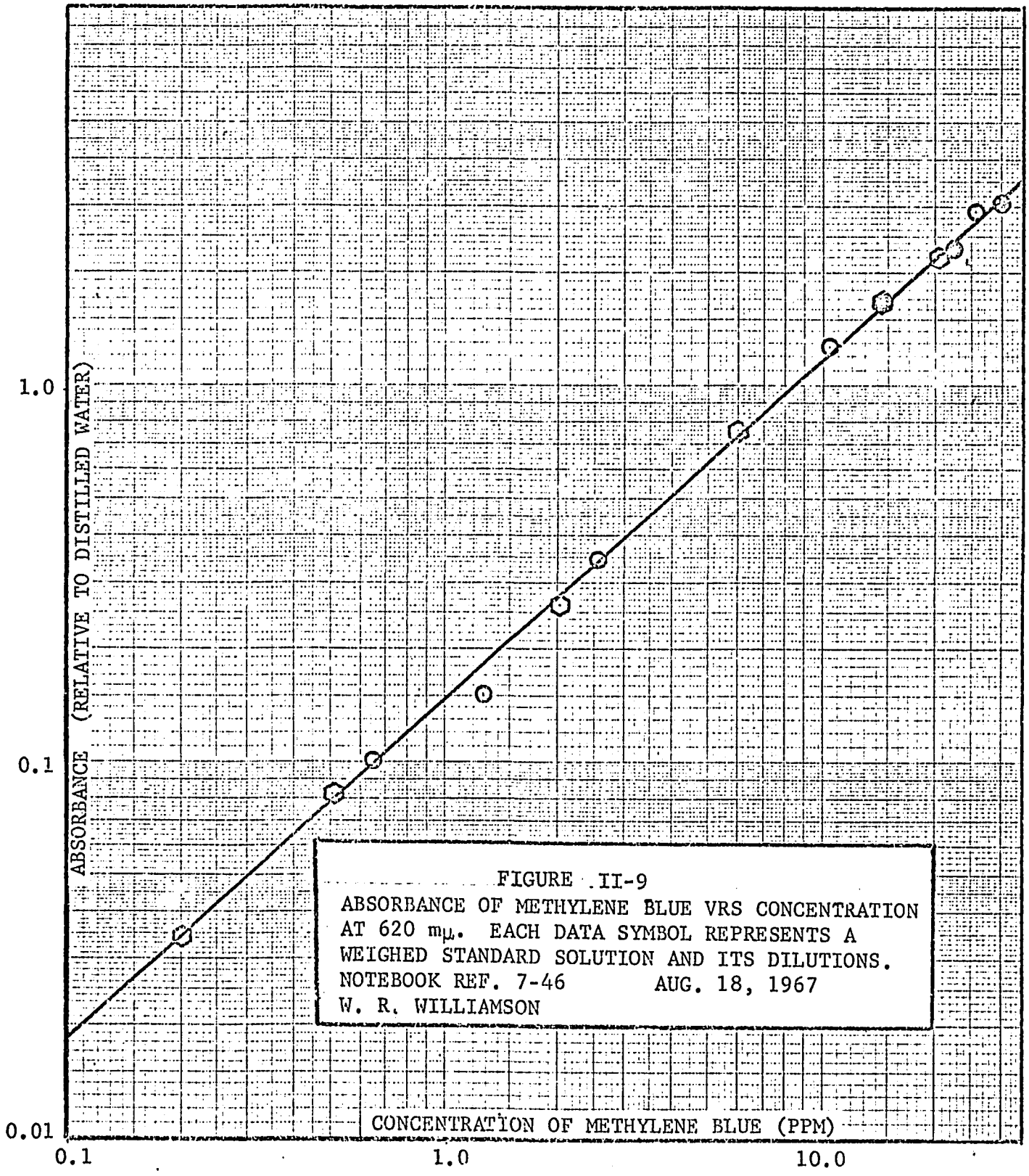

FIGURE II-9
ABSORBANCE OF METHYLENE BLUE VRS CONCENTRATION AT 620 mμ. EACH DATA SYMBOL REPRESENTS A WEIGHED STANDARD SOLUTION AND ITS DILUTIONS.
NOTEBOOK REF. 7-46 AUG. 18, 1967
W. R. WILLIAMSON

The grams of methylene blue absorbed per gram of carbon (X/M) was then calculated for each sample and these values were plotted as a function of the equilibrium concentration of methylene blue. These adsorption isotherms are given in the discussion section. Typical experimental data are given in Table II-2.

It was found that letting the samples stand for 14 hours was not enough to insure that equilibrium had been attained and there was sometimes a slight difference in the amount of adsorption betweem samples left 24 hours and those left for 48 hours. The time required to reach equilibrium could probably have been shortened considerably by constant agitation of the samples but since the color of the samples did not deteriate on prolonged standing at room temperature it was felt that this would offer no important advantages.

TABLE II-2

TYPICAL EXPERIMENTAL DATA FOR ADSORPTION ISOTHERMS

SAMPLE 13-116-A Ground and Sieved through 325 mesh

SOLUTION - 35cc of 2550ppm Methylene Blue Solution

Tube	Carbon (gm)	$Mx10^{-3}$	Dilution	Sensitivity	Measured A_f	Actual A_f	Measured ppm	Actual ppm	X	X/M
A	0.2503	7.14	2:1	4	0.015	1.515	13.7	27.4	2523	354
B	0.2300	6.57	17.6:1	2	0.300	0.800	6.6	116	2434	371
C	0.2102	6.00	41:1	2	0.290	0.790	6.5	267	2283	381
D	0.1904	5.43	101:1	2	0.063	0.563	4.5	455	2095	386
E	0.1704	4.87	101:1	2	0.148	0.648	5.2	525	2025	416
F	0.1501	4.29	101:1	2	0.335	0.835	6.9	697	1853	432
G	0.1305	3.73	101:1	3	0.046	1.046	8.9	899	1651	442
H	0.0907	2.59	101:1	4	0.045	1.545	13.7	1385	1165	450

CHAPTER II

REFERENCES

1. Madison, J. J., Analyt. Chem., 30, No. 11, 1859 (1958).

2. Fleury, P., and Lang, J., J. Pharm. Chim., 17, No. 8, 107 (1933).

3. Jackson, E. L., Organic Reactions, vol. 2, John Wiley and Sons, New York (1944).

4. Rieman, W., Neuss, J. D., and Naiman, B., Quantitative Analysis, 3rd Ed., McGraw-Hill Book Co., New York (1951).

Chapter III

DISCUSSION OF RESULTS

General Discussion

As stated in the Introduction this work was conceived as being the first in a continuing program of investigations into the use of thermal and catalytic means to obtain useful chemicals from cellulosics. Consequently the equipment was built to be as versatile as possible as described in the Experimental Section. Initial efforts were aimed at discovering a variety of potentially fruitful areas of research. The results of these investigations are described in the "Batch Pyrolysis Reaction" and "Continuous Pyrolysis Reaction" sections which follow. In the course of these investigations the theory for the new process for the manufacture of activated carbon described in the Introduction was conceived. The remainder of the work covered in this paper then concerned itself with the confirmation and evaluation of this theory.

Batch Pyrolysis Reaction

The batch pyrolysis reactions were divided into three groups:

1. Batch feed of bagasse pith with continuous feed of steam throughout the run.
2. Batch feed of bagasse pith with no steam feed.
3. Batch feed of bagasse pith with rapid heat-up of the reaction mixture accomplished by preheating the reactor heaters before inserting the filled reactor.

In these experiments the quantity of liquid and gaseous overhead products was measured. The liquid product was titrated with a sodium hydroxide solution to a neutral end point and the amount of

acid products (expressed as grams of acetic acid) was calculated. The gas was analized using gas chromatography.

The yield of total acid as a function of the final reaction temperature is shown graphically in Figure III-1 and the data are given in Table III-1. The data show that the acid yield decreases slightly with increased reaction temperature as would be expected since thermodynamics favors the formation of CO, CO_2 and H_2O at higher temperatures. Somewhat surprisingly, however, the acid yield appears to be relatively unaffected by the heat-up rate or the addition of steam to the reactor. The time interval over which the acid-producing reaction is observed is prolonged by the addition of steam and is reduced by an increase in the heat-up rate as shown by a comparison of Figures III-2, 3, 4 and 5 with Figures III-6 and 7 and with Figures III-8, 9, 10 and 11. Experimental data are tabulated in Appendix A. These figures show the rate of formation of acid products and the average reaction temperature as a function of time. Comparison of the figures reveals a definite change in the slope of the curves in going from one set of experiments to another but little change in slope within a particular set of experiments. Summarizing these results it appears that the rate at which acid products are formed is enhance by an acceleration of the heat-up rate and by a decrease in the partial pressure of water in the reactor atmosphere while the yield of acid products is relatively unaffected by these variables.

The yield of gaseous products, however, is appreciably increased by the addition of steam to the reactor as shown in Figure III-12. Data for this figure are given in Table III-1. This figure confirms the thermodynamic prediction of an increase in gaseous

TABLE III - 1

EXPERIMENTAL DATA ON PRODUCT YIELDS
FOR BATCH PYROLYSIS OF BAGASSE PITH

FINAL REACTION TEMPERATURE	TOTAL ACID YIELD (1)	GAS YIELD (2)	SOLID RESIDUE YIELD (3)	STEAM FEED RATE (4)	TYPE OF HEAT UP
330	6.6	2.7×10^{-3}	37.7	0.725	SLOW
410	5.2	3.4×10^{-3}	*	0.257	SLOW
510	5.6	5.6×10^{-3}	36.7	0.278	SLOW
690	5.6	12.7×10^{-3}	32.6	0.334	SLOW
718	4.3	5.7×10^{-3}	35.4	0	SLOW
730	5.7	6.1×10^{-3}	29.9	0	SLOW
295	*	0.2×10^{-3}	36.1	0	RAPID
460	5.2	2.24×10^{-3}	26.9	0	RAPID
470	6.0	2.41×10^{-3}	27.6	0	RAPID
535	5.1	2.22×10^{-3}	24.7	0	RAPID
605	7.7	2.78×10^{-3}	19.9	0	RAPID

* THESE DATA NOT OBTAINED

(1) CALCULATED AS GM. OF ACETIC ACID/GM. OF BAGASSE PITH FED

(2) $FT.^3$/GM. OF BAGASSE PITH FED

(3) GM./GM. OF BAGASSE PITH FED

(4) GM./MIN./GM. OF BAGASSE PITH FED

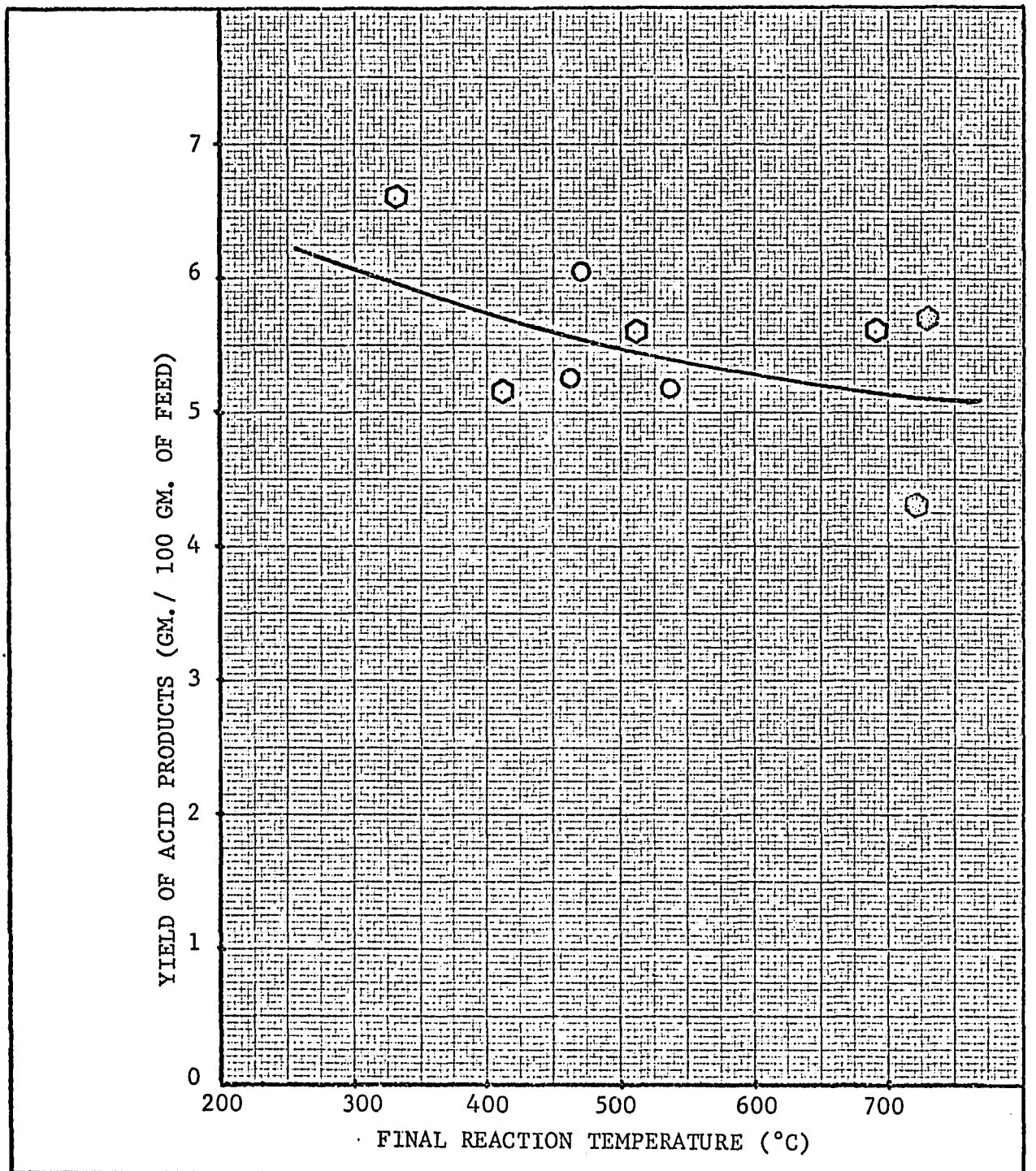

FIGURE III - 1

YIELD OF TOTAL ACID EXPRESSED AS ACETIC ACID AS A FUNCTION OF FINAL REACTION TEMPERATURE FOR THE BATCH PYROLYSIS OF BAGASSE PITH.

⬡ SLOW HEAT UP WITH STEAM FEED

⬢ SLOW HEAT UP WITHOUT STEAM FEED

○ RAPID HEAT UP WITHOUT STEAM FEED

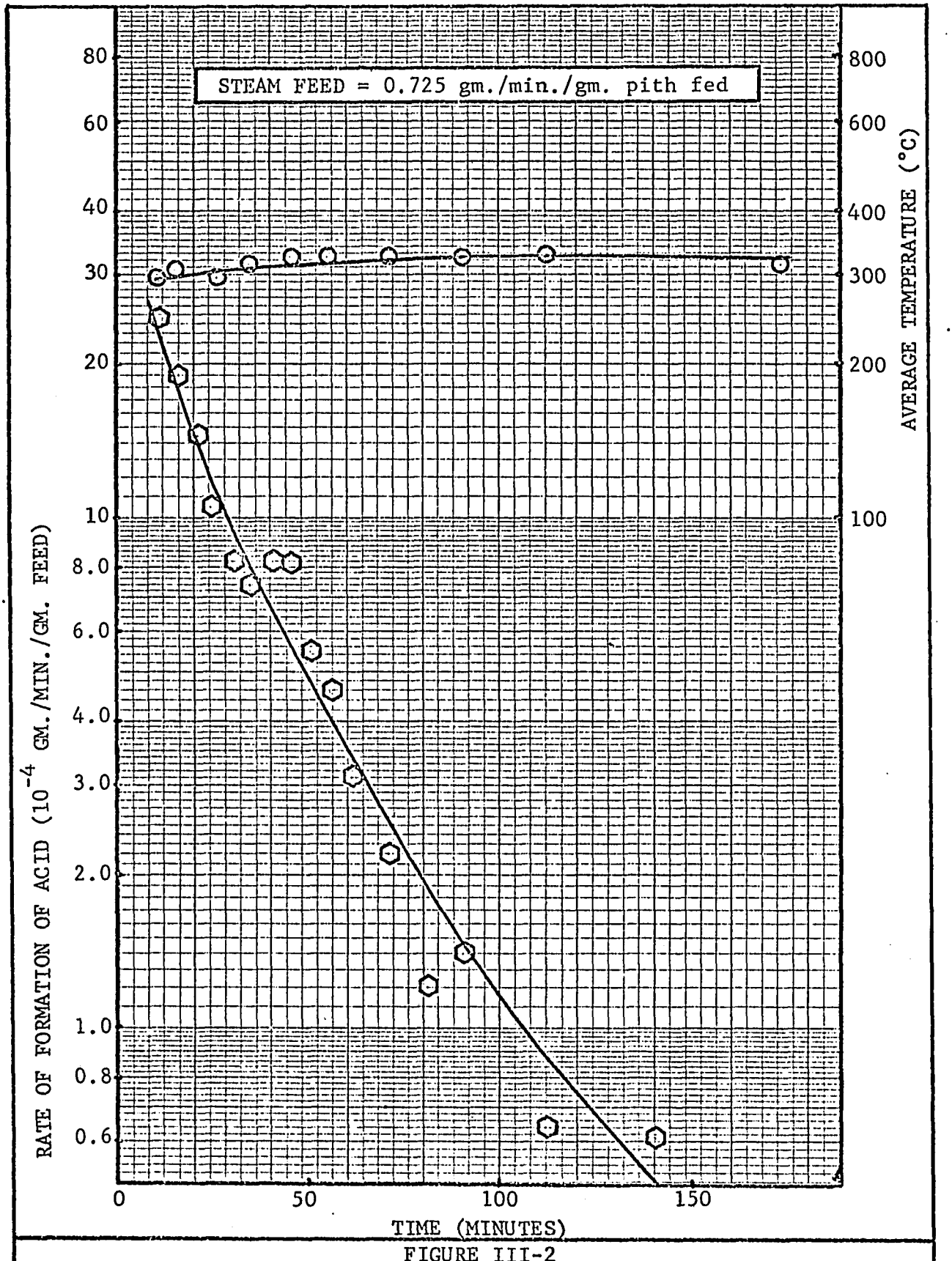

FIGURE III-2

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH STEAM FED CONTINUOUSLY DURING REACTION.

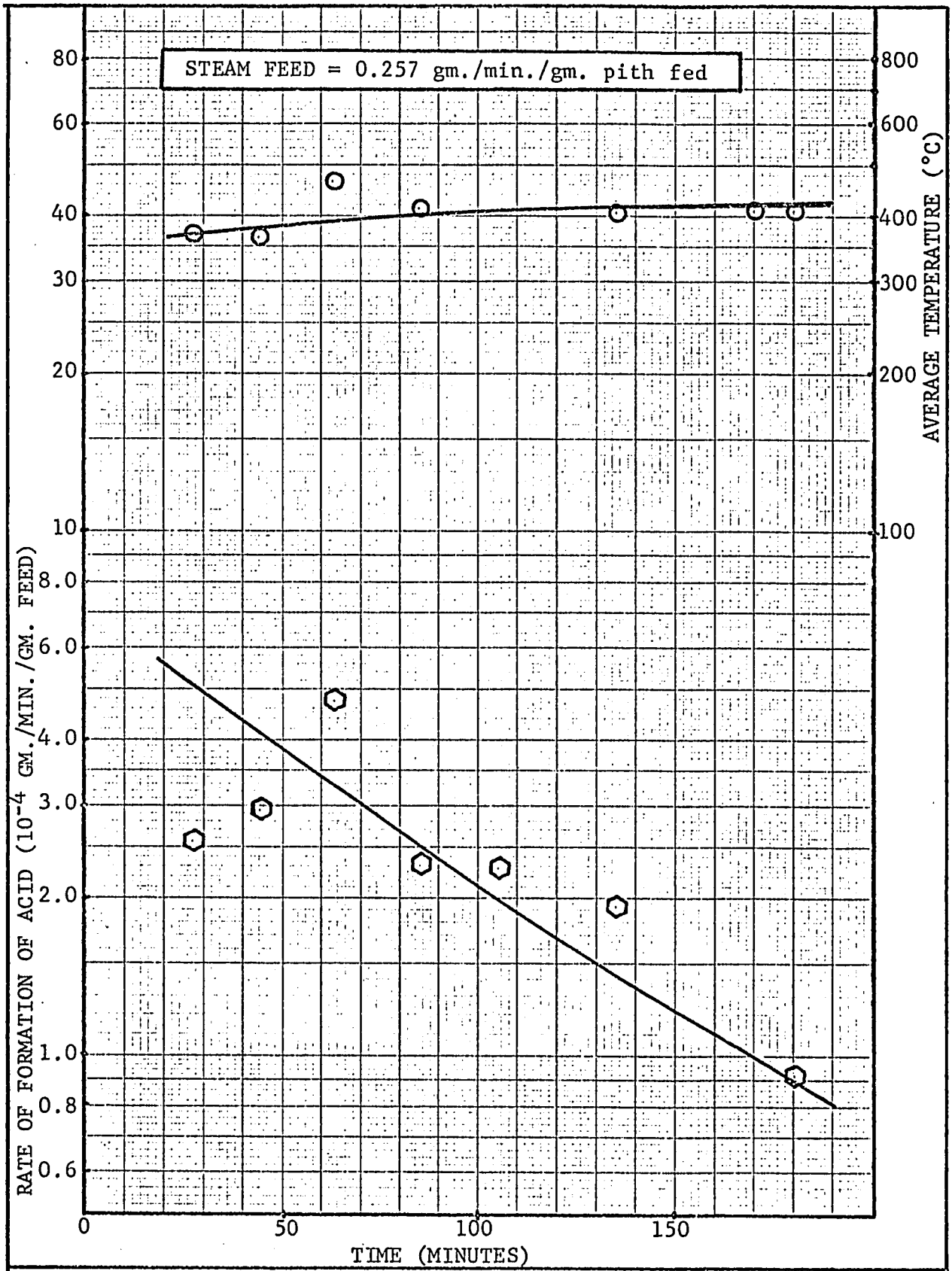

FIGURE III - 3

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH STEAM FED CONTINUOUSLY DURING REACTION.

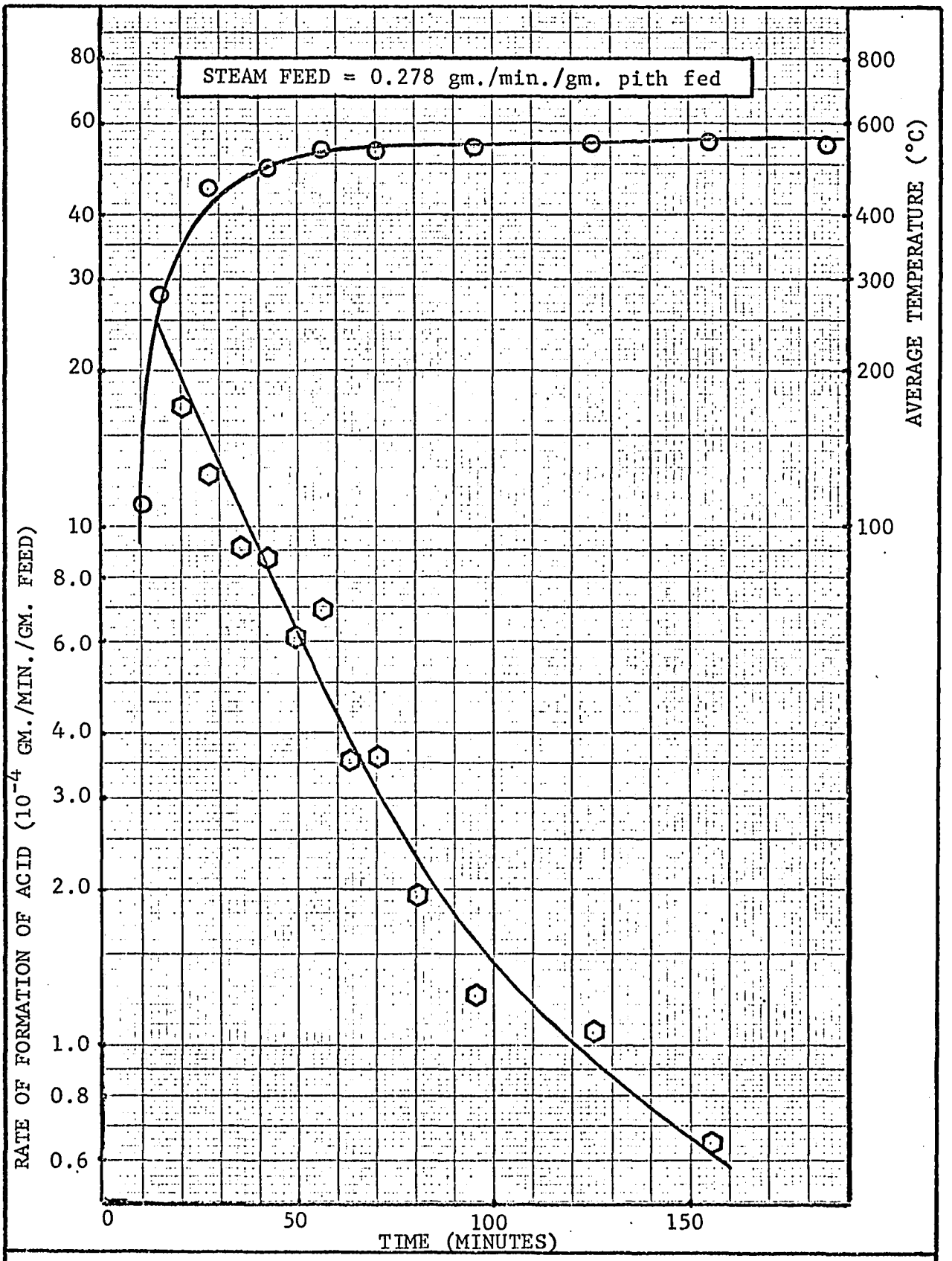

FIGURE III - 4

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH STEAM FED CONTINUOUSLY DURING REACTION.

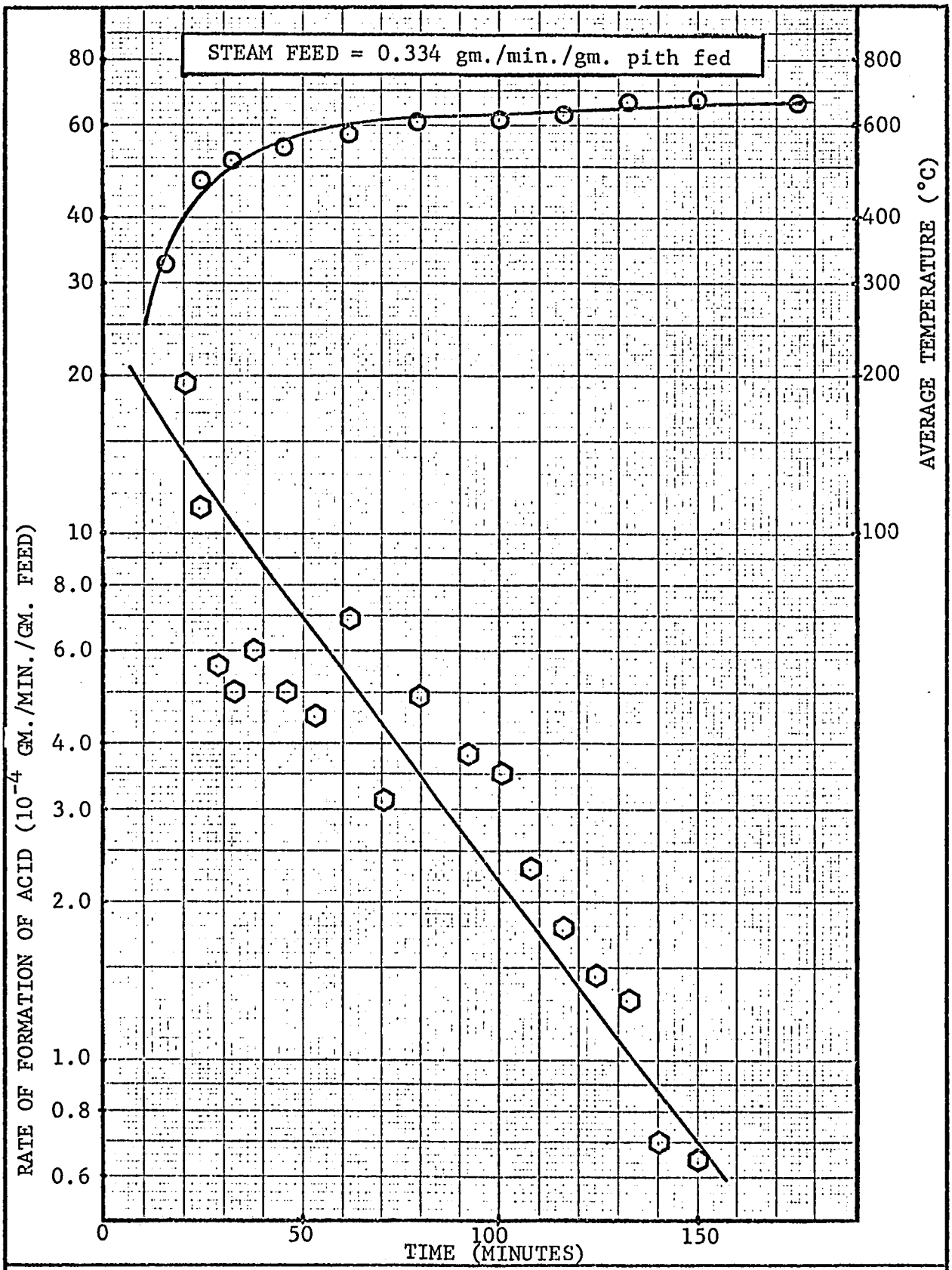

FIGURE III - 5

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH STEAM FED CONTINUOUSLY DURING REACTION.

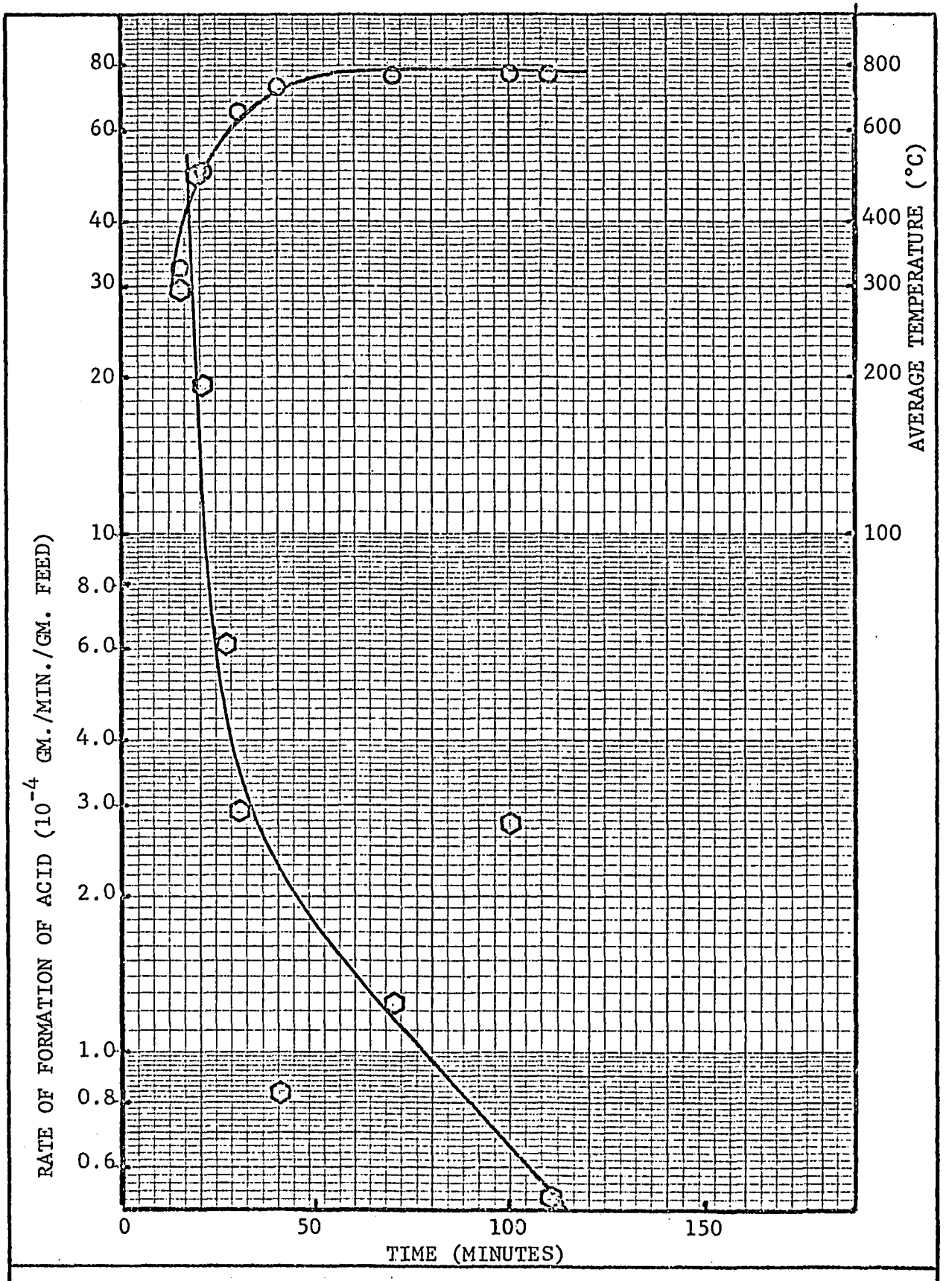

FIGURE III - 6

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND SLOW HEAT UP.

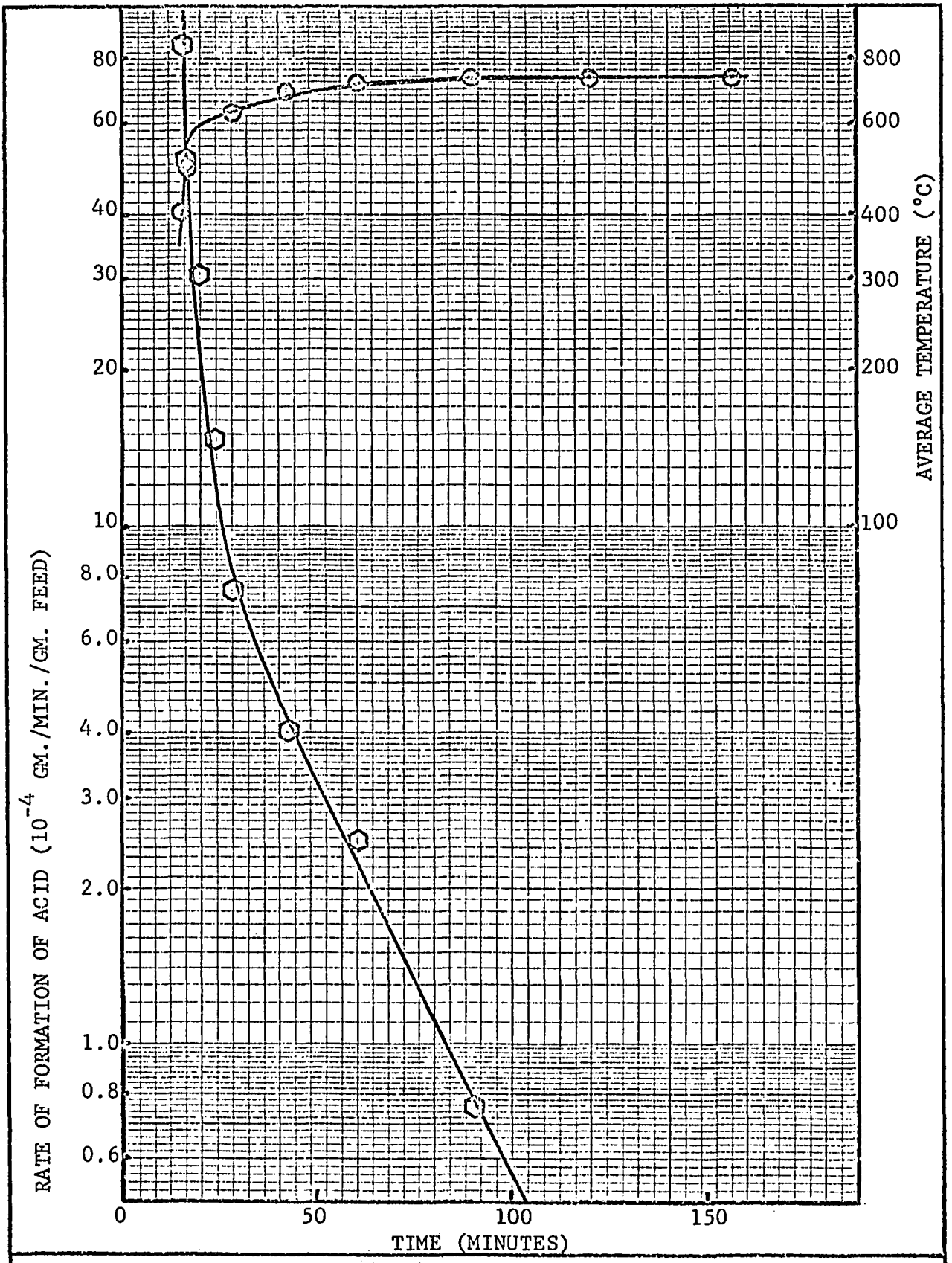

FIGURE III - 7

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND SLOW HEAT UP.

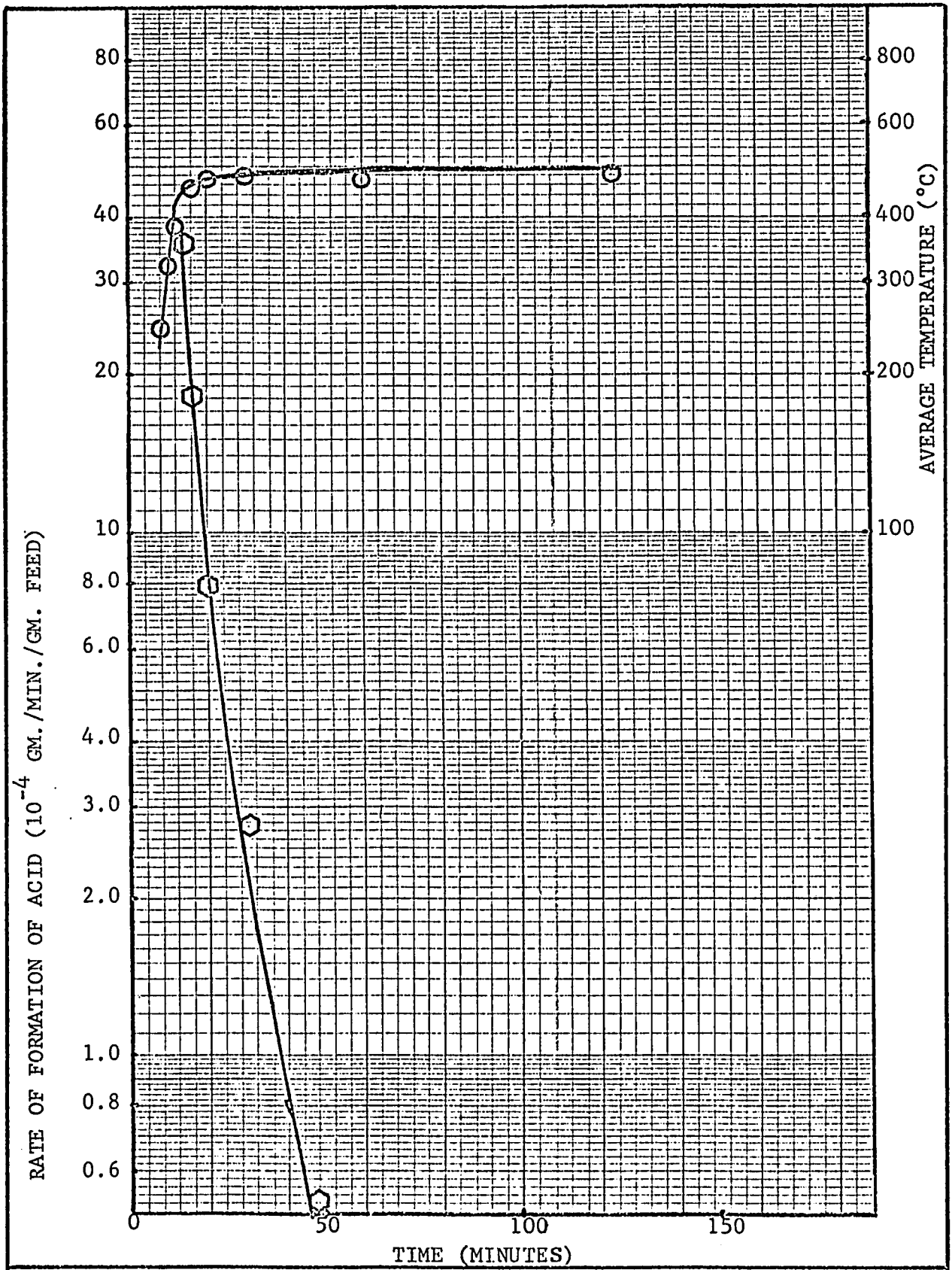

FIGURE III - 8

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND RAPID HEAT UP.

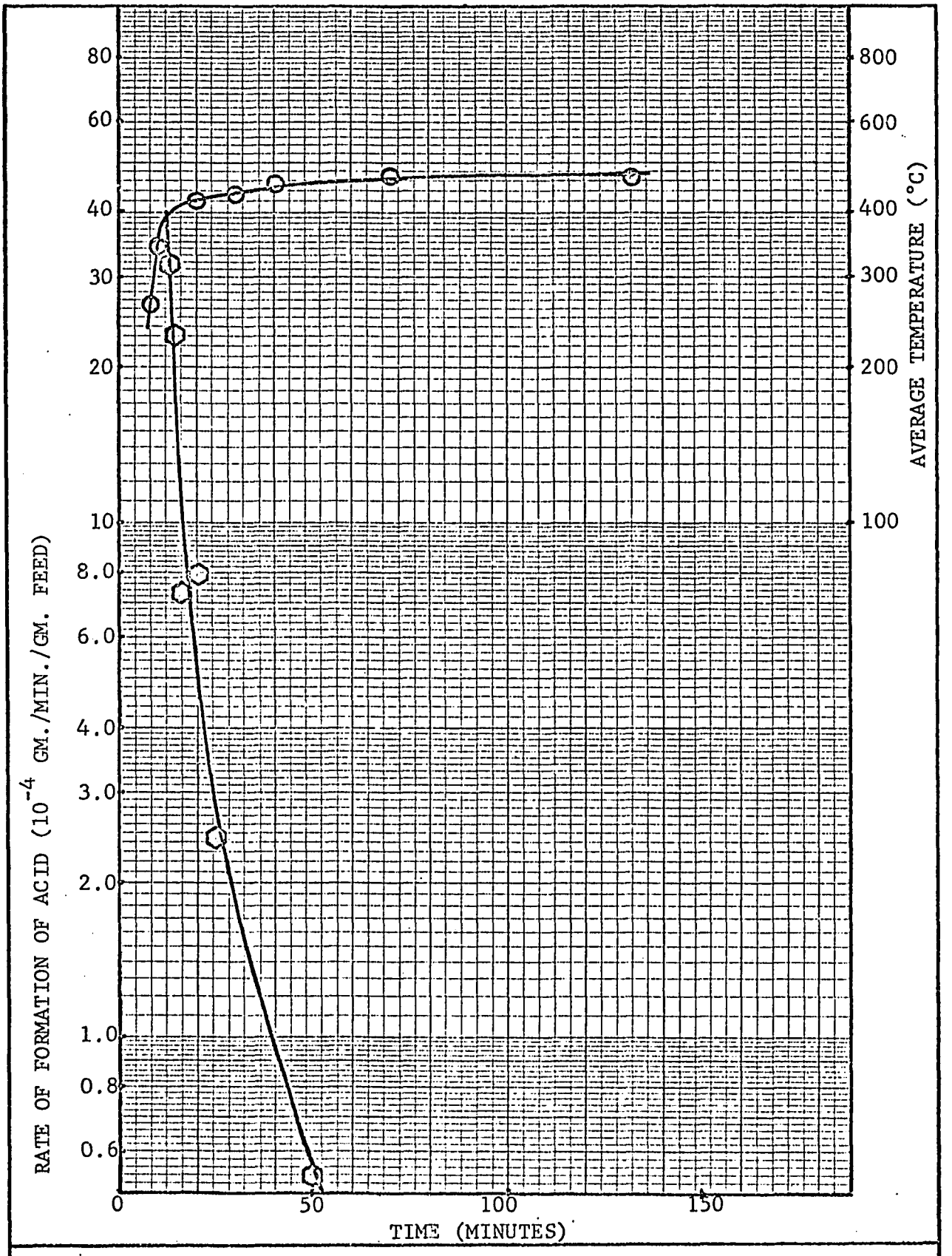

FIGURE III - 9

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND RAPID HEAT UP.

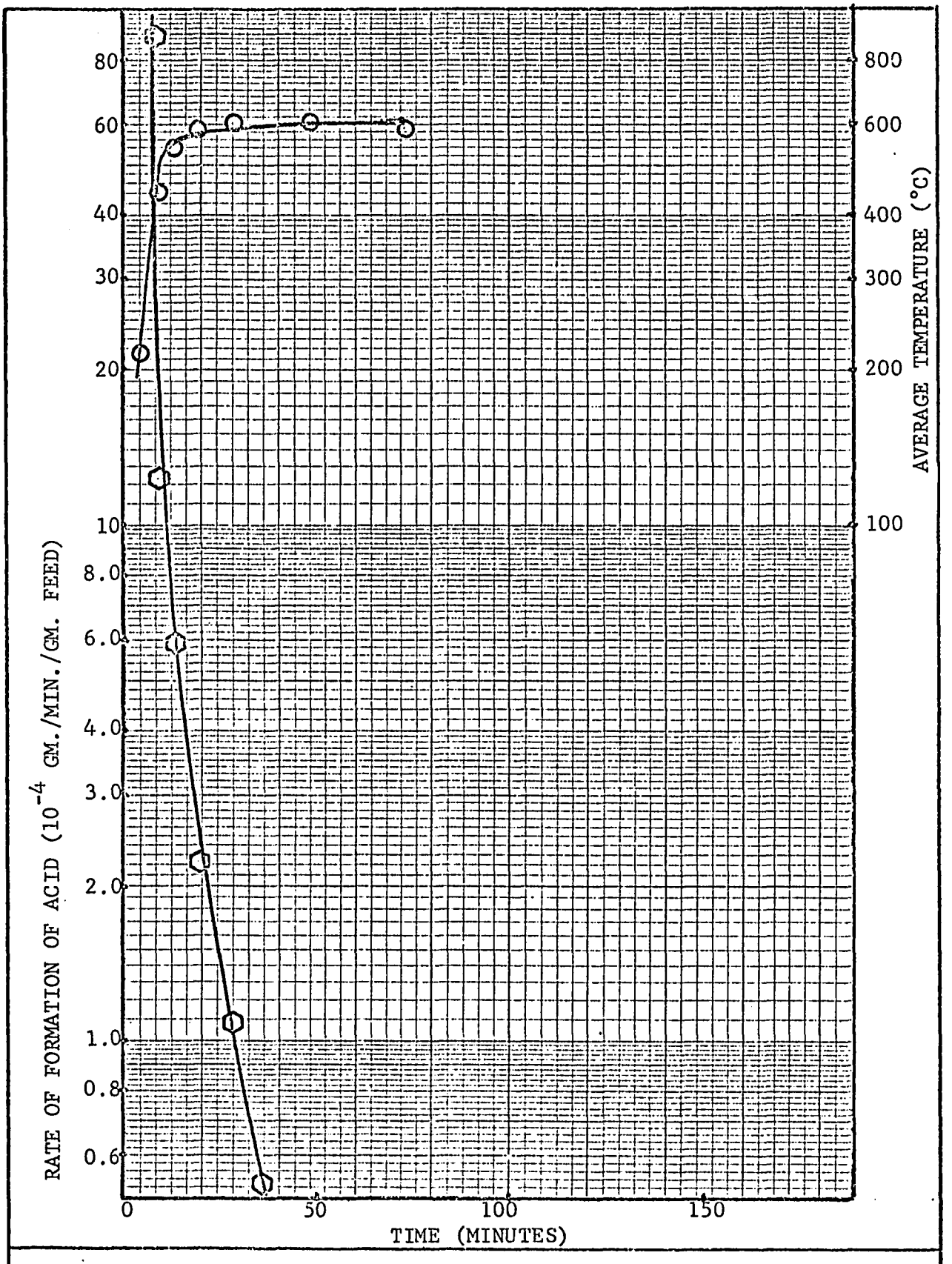

FIGURE III - 10

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND RAPID HEAT UP.

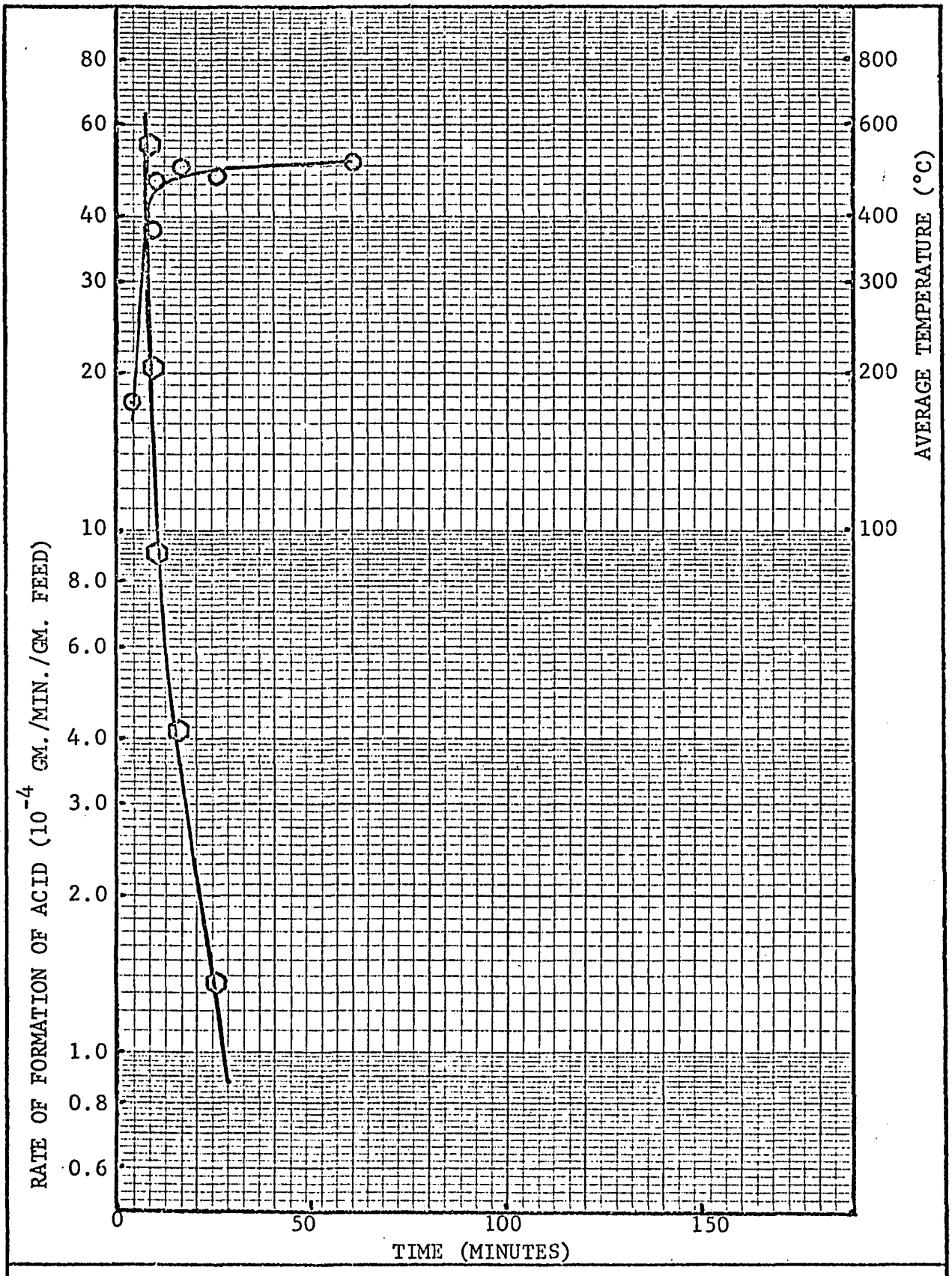

FIGURE III - 11

RATE OF FORMATION OF ACID PRODUCTS (EXPRESSED AS ACETIC ACID) AND AVERAGE REACTION TEMPERATURE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND RAPID HEAT UP.

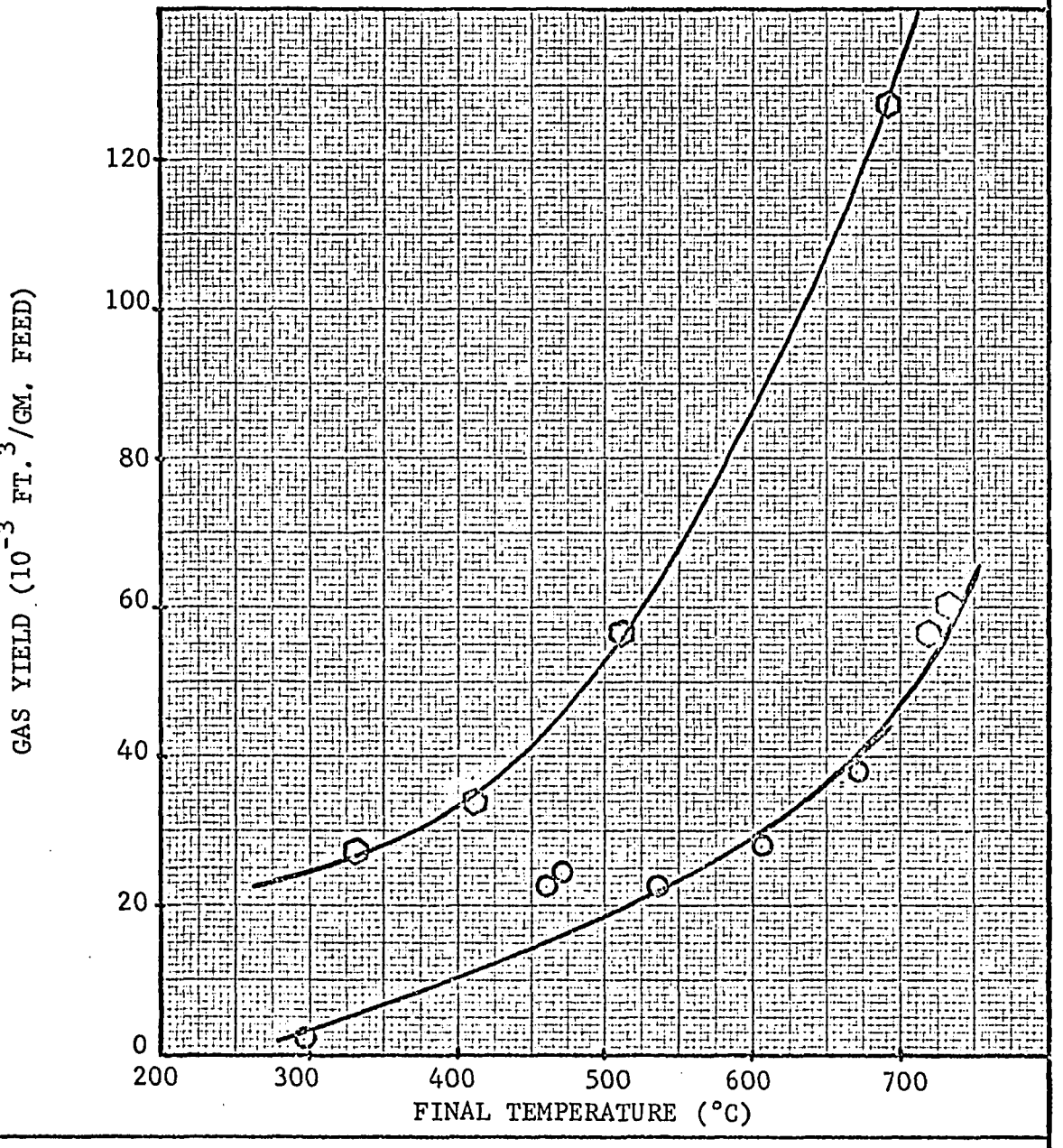

FIGURE III - 12

YIELD OF GAS AS A FUNCTION OF FINAL REACTION TEMPERATURE FOR BATCH PYROLYSIS OF BAGASSE PITH.

⬡ SLOW HEAT UP WITH STEAM FEED

⬡ SLOW HEAT UP WITHOUT STEAM FEED

○ RAPID HEAT UP WITHOUT STEAM FEED

products with increasing reaction temperature mentioned previously. The rate of heating appears to have little affect on the gas yield.

The variation of gas composition (dry basis) and the rate of formation of gaseous products as a function of time is shown in Figures III-13, 14, 15 and 16. Data points were eliminated from Figures III-14, 15, and 16 to improve readability. These experimental data are tabulated in Appendix A. The scatter in data points shown in Figure III-13 is typical of the other runs also. Comparison of Figures III-15 and 16 shows that, while the yield of gaseous products is not affected by the heat-up rate, the rate of formation of these products is increased by an increase in the heat-up rate.

In all of the runs the gas composition approached constant values late in the run. This is not too apparent for the rapid heat-up experiment (Figure III-16) but this is because the gas rate dropped so quickly that it was not possible to obtain successive samples late in the run. The equilibrium composition in each case resembles that which one would obtain from the reaction of steam with carbon, that is, a high concentration of hydrogen, carbon dioxide, and carbon monoxide. The methane concentration is higher than one would expect, however, since temperatures less than 400°C are normally utilized for its formation via a Fischer-Tropsch reaction (1). At even higher temperatures (greater than 750°C) the reaction of carbon with steam would yield a higher ratio of carbon monoxide to carbon dioxide.

Figures III-17 shows the effect of rate of heating and of final reaction temperature on the yield of solid residue, the data are given in Table III-1. A rapid heat-up seems to produce a lower yield of solid residue for the same final reaction temperature. The

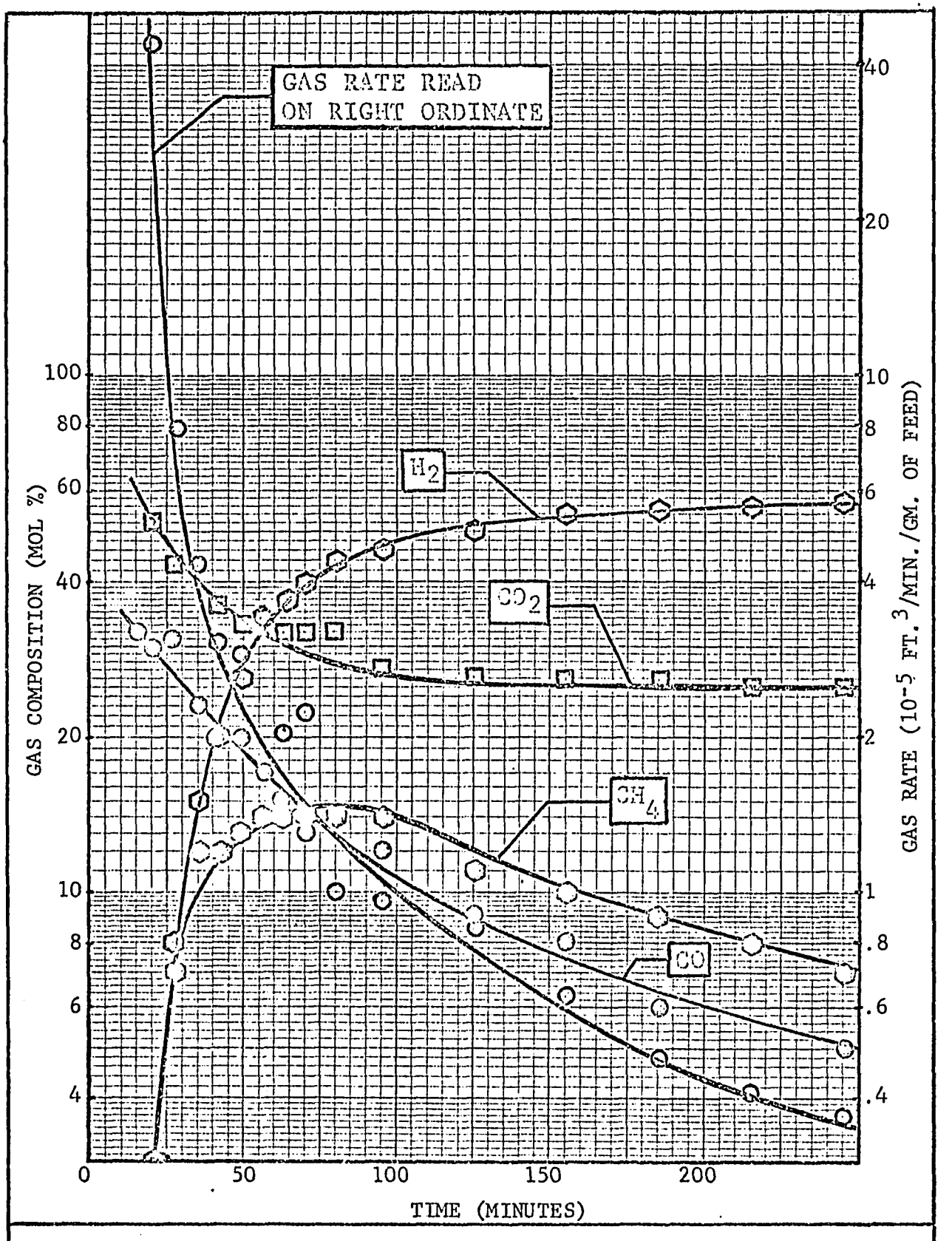

FIGURE III - 13

GAS COMPOSITION AND GAS RATE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH STEAM FED CONTINUOUSLY THROUGHOUT REACTION. FINAL TEMPERATURE WAS 510°C.

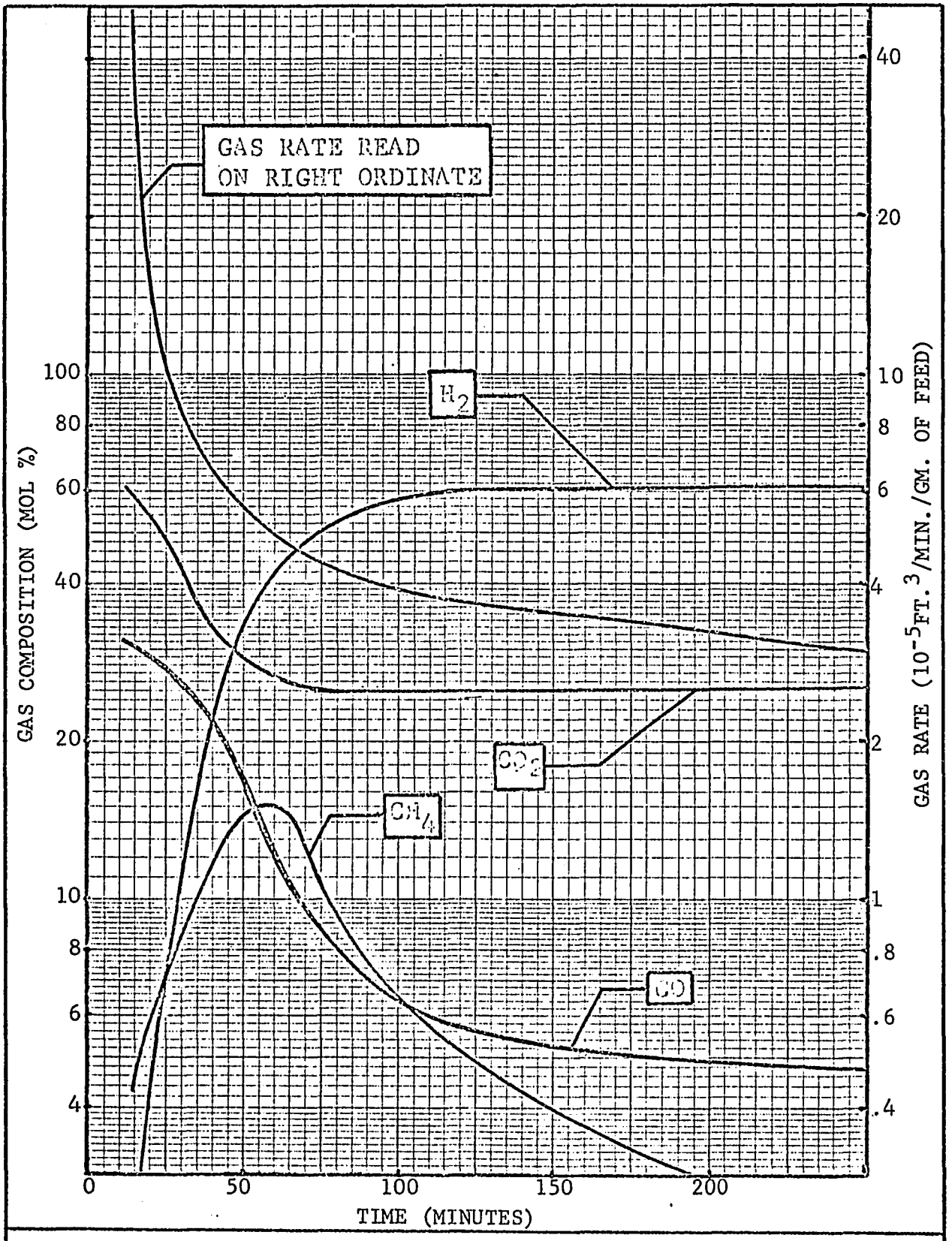

FIGURE III - 14

GAS COMPOSITION AND GAS RATE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH STEAM FED CONTINUOUSLY THROUGHOUT REACTION. FINAL TEMPERATURE WAS 690°C.

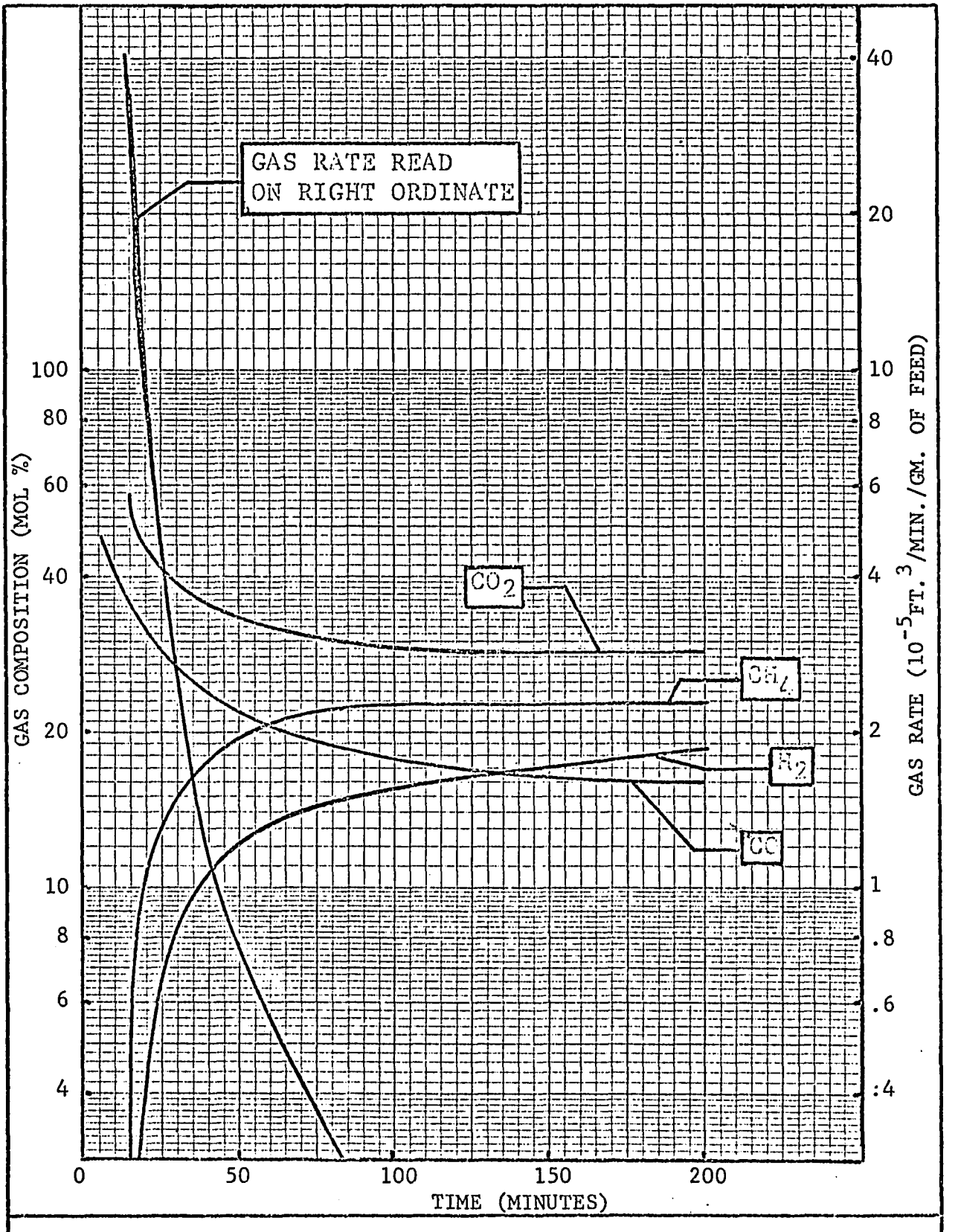

FIGURE III - 15

GAS COMPOSITION AND GAS RATE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND SLOW HEAT UP RATE. FINAL TEMPERATURE WAS 530°C.

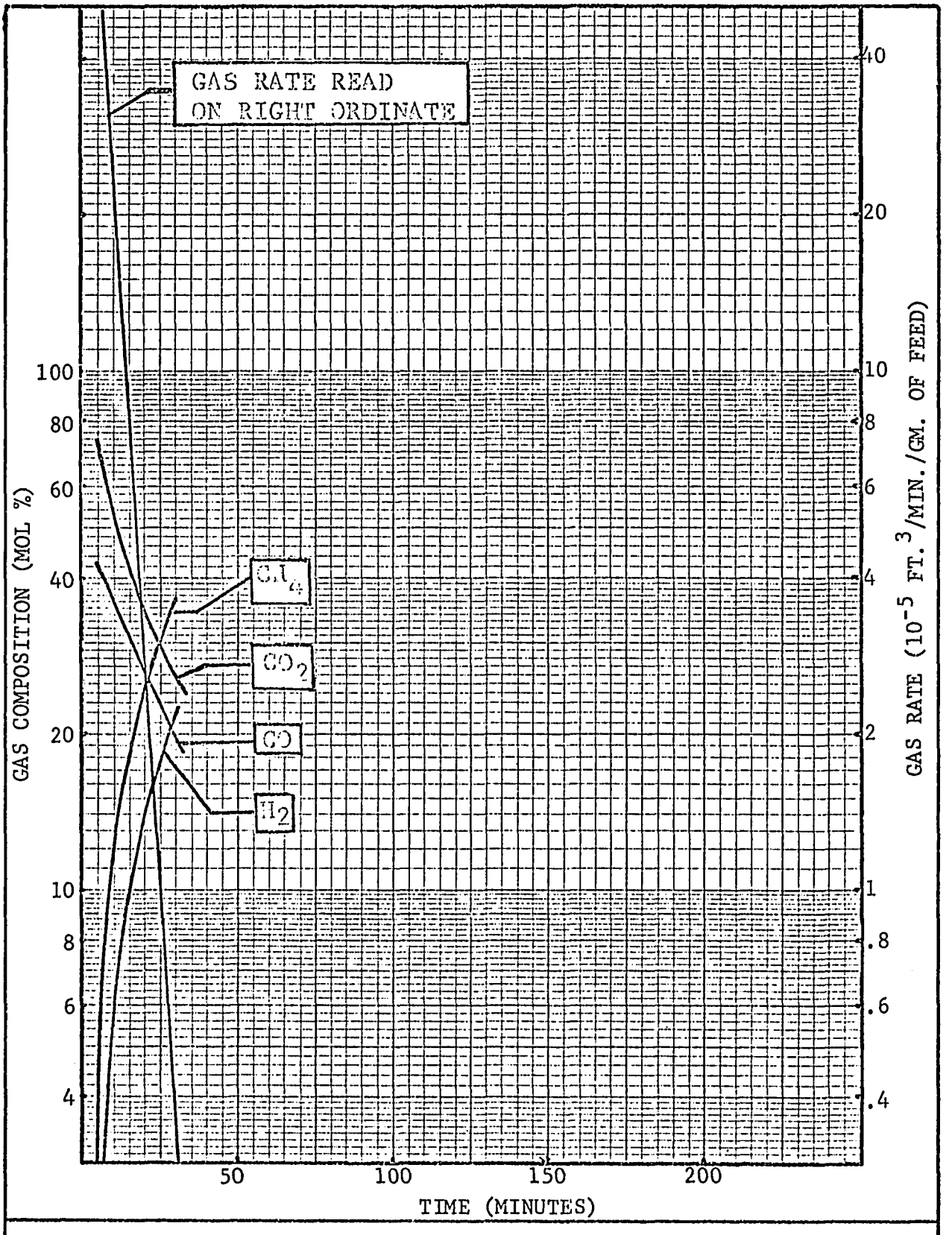

FIGURE III - 16

GAS COMPOSITION AND GAS RATE AS A FUNCTION OF TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED AND RAPID HEAT UP. FINAL TEMPERATURE WAS 605°C.

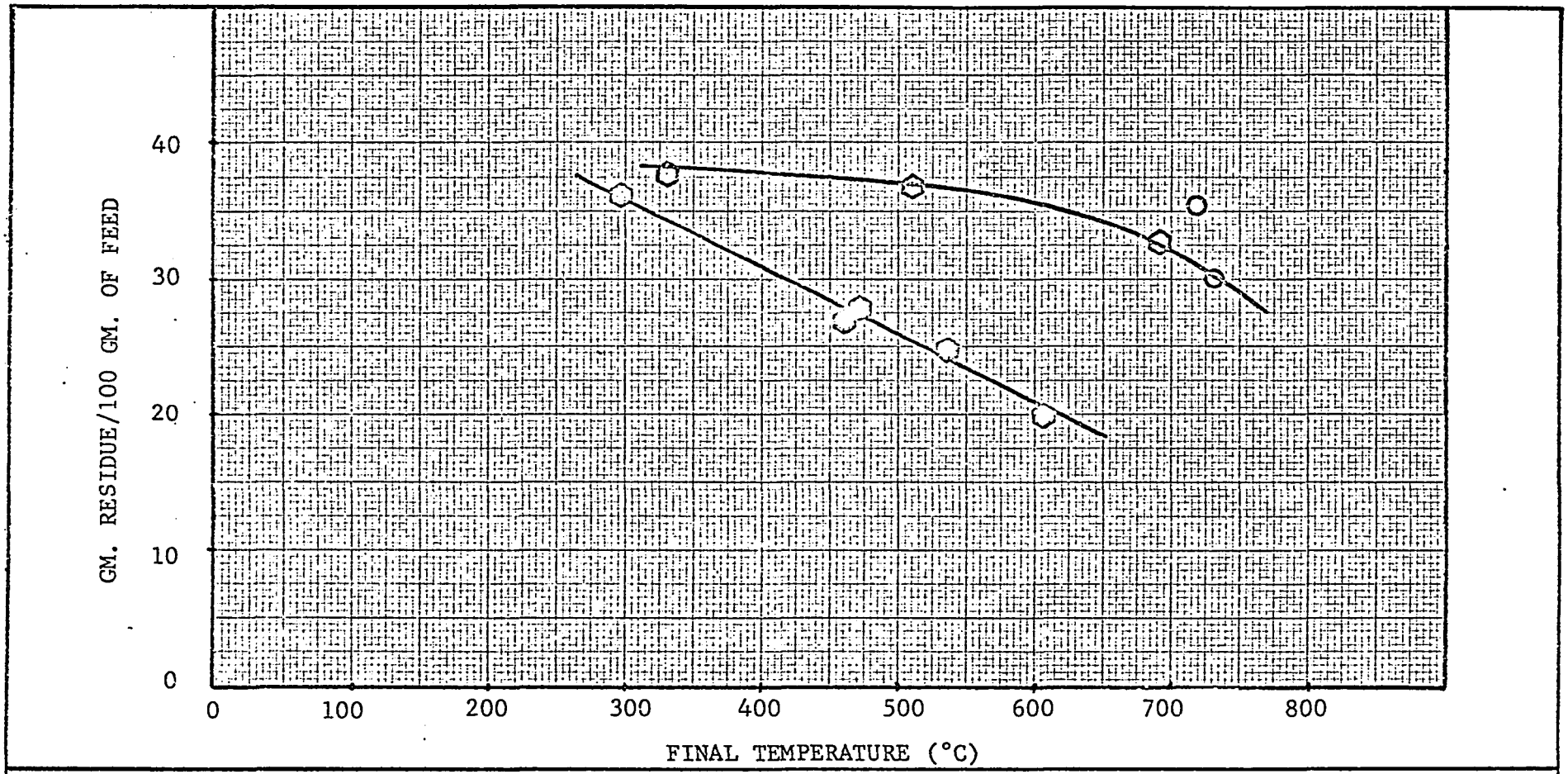

FIGURE III - 17

YIELD OF SOLID RESIDUE AS A FUNCTION OF FINAL REACTION TEMPERATURE FOR BATCH PYROLYSIS OF BAGASSE PITH.

⬡ SLOW HEAT UP WITH STEAM FEED
○ SLOW HEAT UP WITHOUT STEAM FEED
⬡ RAPID HEAT UP WITHOUT STEAM FEED

addition of steam did not affect the yield of residue. This is in conflict with previous data which indicates that the steam is reacting with the residual carbon to produce gaseous products. This anomaly is explained by the fact that all reactions were shut down shortly after liquid products ceased to be observed. When steam was being fed, the run was stopped when no more acid products were detected in the overhead condensate. It is obvious from the gas rate data given in Figures III-13 and 14 that continued reaction with steam feed would result in very little yield of solid residue since the reaction of the steam with the residual carbon would be expected to go essentially to completion.

The per cent of the cellulose feed that had reacted at various times during the run was calculated by summing the amounts of overhead products. Plots of these values as a function of reaction time for two of the rapid heat-up runs are given in Figures III-18 and 19. The experimental data are given in Appendix A. The fact that these data yield a straight line up to about 60% reacted (85% of the total reaction that occurred) indicates that the reaction has an overall order of zero. Levenspiel (2) shows that the equation to represent this type of reaction is:

$$X = \frac{k}{C_{Ao}} t$$

where X = fraction reacted

k = reaction rate constant

C_{Ao} = initial concentration of reactant

t = time

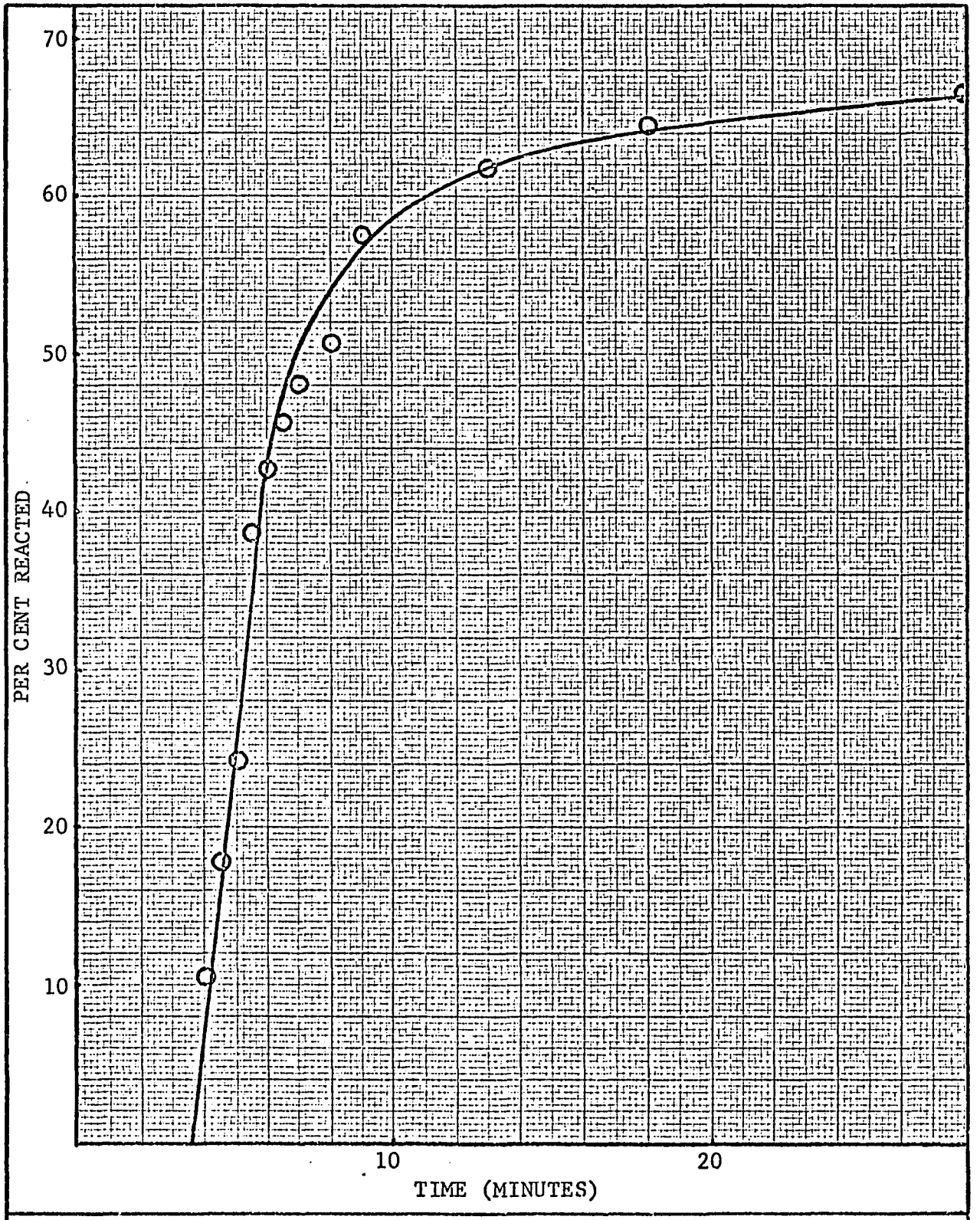

FIGURE III - 18

PER CENT REACTED VS TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH RAPID HEAT UP TO A FINAL TEMPERATURE OF 605°C.

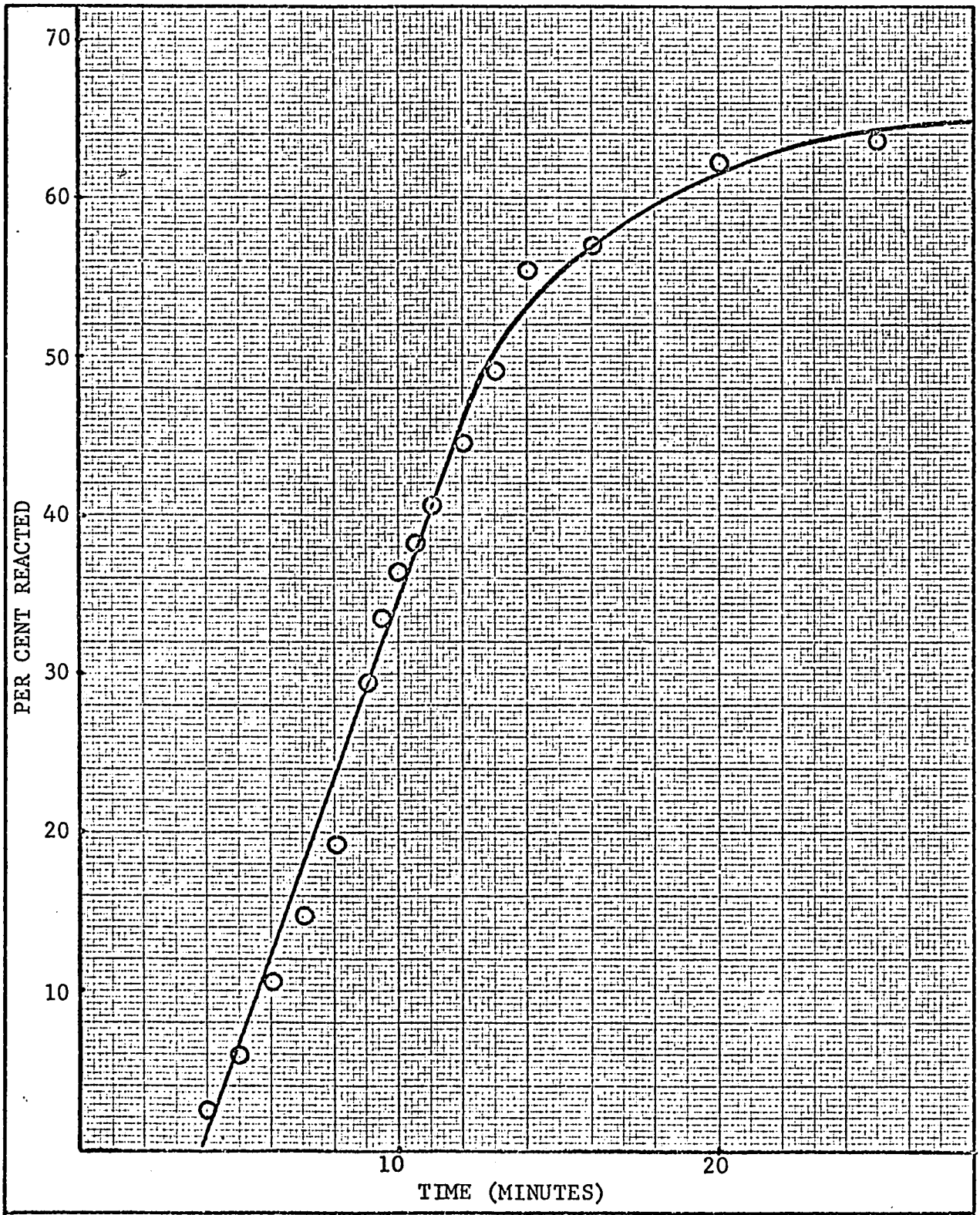

FIGURE III - 19

PER CENT REACTED VS TIME FOR BATCH PYROLYSIS OF BAGASSE PITH WITH RAPID HEAT UP TO A FINAL TEMPERATURE OF 460°C.

This is the equation of a straight line with intercept at the origin and slope equal to k/C_{Ao}. It is obvious that the initial data of Figures III-18 and 19 fit this equation except for the intercept requirement. The fact that the intercept does not occur at the origin for the experimental data can be explained by the fact that the per cent reacted was calculated by measuring the quantity of overhead products. There would certainly be some time lag involved in collecting these samples. Also, since a finite time was required to heat the reactants, some time lag between the insertion of the reactor into the heaters and the appearance of reaction products would be expected.

Neglecting, then, the fact that the intercept of the experimental data was not at zero time, the initial slope of the per cent reacted vs. time curves were calculated. For the 605°C final reaction temperature experiment (Figure III-18) the slope was found to be 0.178 ($min.^{-1}$) and for the 460°C case (Figure III-19) the slope was 0.0562 ($min.^{-1}$). Using the empty volume of the reactor (8.0×10^{-3} $ft.^3$) and the amount of pith fed to calculate the initial concentrations gives values of the reaction rate constant, k, of 0.223 ($ft.^3/gm.\text{-}min.$) and 0.0609 ($ft.^3/gm.\text{-}min.$) for the 605°C and 460°C experiments respectively. This is a rather small difference considering the large difference in temperature and indicates that the time required to heat the reacting mixture up to the final temperature is quite large compared with the reaction time. Consequently the rate constants obtained are probably not representative of the final temperatures but of some intermediate average temperature that would be representative of the unsteady temperature conditions prevailing during the heat-up period.

Furthermore the assumption of zero order kinetics may also be in error.

Continuous Pyrolysis Reaction

In the design of continuous reactors for solid materials which produce gaseous reaction products two major problems are the introduction of the solid feed and removal of the solid reaction products. In this study the first of these problems was overcome by using the solids feed valve described in Chapter II. Since a slight positive pressure is generated in the reactor it was found necessary to feed the bagasse pellets from a sealed reservoir. If an open reservoir was used the vapors generated in the reaction would flow backwards through the solids feed valve instead of flowing through the recovery and analysis system.

A study of the batch reaction data showed that the decomposition reaction proceeds essentially to completion quite rapidly at temperatures above 350°C. This suggested a method of circumventing the problem of continuous removal of the solid residue in the continuous reaction. It was reasoned that if the reactor were fed continuously and no solid products were removed that a steady state in the amount and composition of the overhead products would be quickly reached. The batch data indicated that the solids residing in the reactor for a period greater than about forty minutes would be essentially inert if no steam feed were employed. Consequently, the experimental runs were conducted with continuous feed and continuous overhead product removal but with no removal of solid residue. The amount of overhead products and the composition of the product gas were measured periodically. When these quantities reached steady state, it was assumed that they were the same as they would be if

solid product removal were employed.

A typical gas composition-time profile is shown in Figure III-20. The experimental data for this run and for the other experiments is given in Appendix B. These data indicate that a feed period of about 50 minutes is required before a constant gas composition is attained. Figure III-21, however, shows that only 10-15 minutes are required before the rate of gas formation reaches a steady value except for the low temperature (330°C) run where an interval of 20 minutes was required. The data for the start-up period for the 630°C run shown in this figure were eliminated from the figure because the feed during this period was erratic due to bridging in the reactor. This problem was cleared up by beating on the reactor with a hammer a few times, after which the feed was quite steady. Only data for the period of steady operation have been shown. All of the experimental data are tabulated in Appendix B.

The effect of temperature on the steady state gas composition is shown in Figure III-22 and Table III-2. The high methane and low hydrogen yield observed in the batch reactions with no steam feed are also observed in these data. Comparison of Figure III-22 with Figures III-15 and 16 shows that the steady state gas compositions obtained in the continuous reaction correspond most closely with the compositions obtained during the initial portion of the batch reactions.

The steady state gas yield was obtained by dividing the gas production rate at steady state by the average feed rate. These data are given in Figure III-23 and Table III-3. Comparison of these data with the gas yield data for the batch runs given in Figures III-12

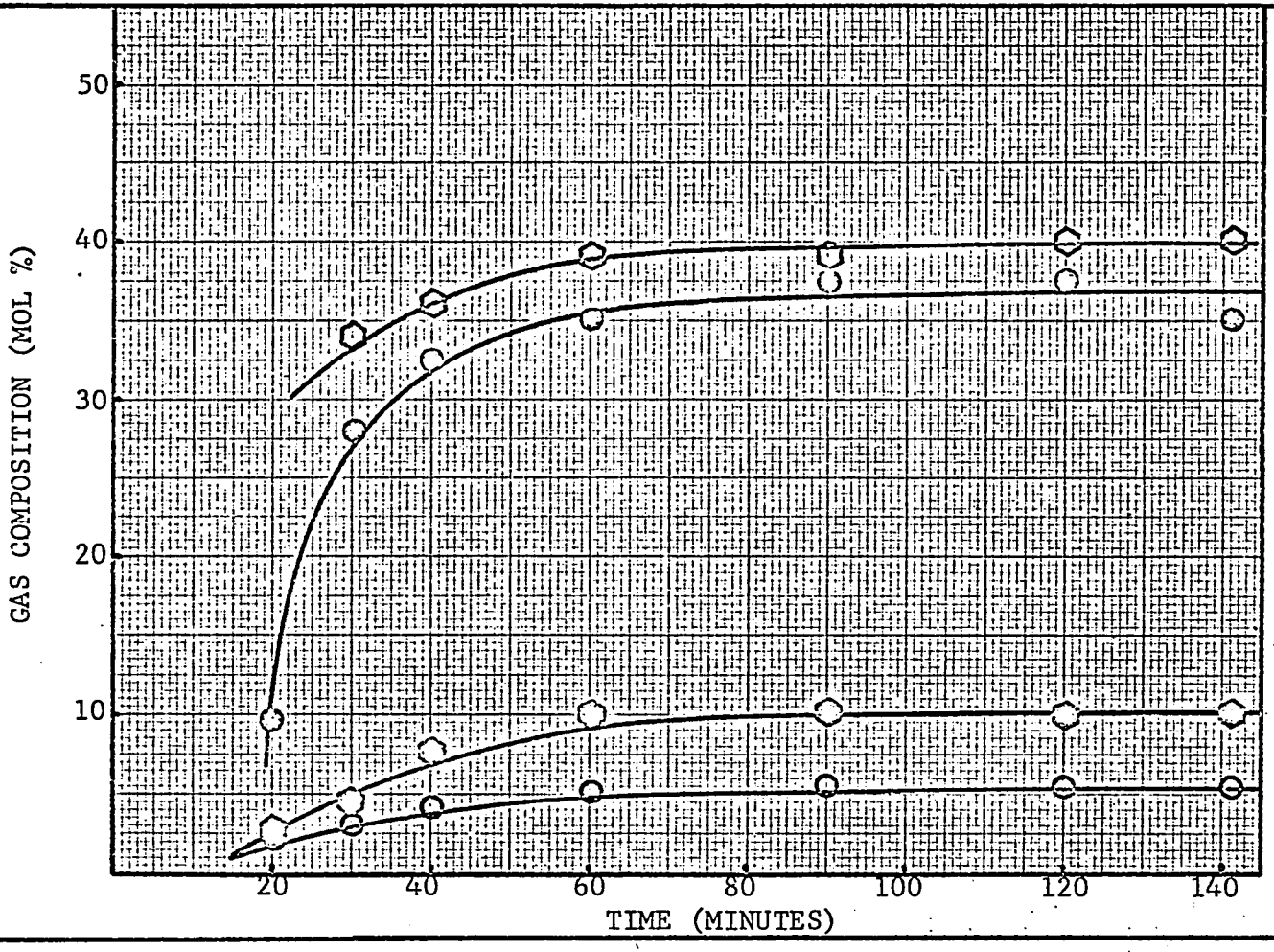

FIGURE III - 20

GAS COMPOSITION AS A FUNCTION OF TIME FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED. REACTION TEMPERATURE WAS 510°C. AVERAGE FEED RATE WAS 0.616 GM./MIN.

- CARBON MONOXIDE
- CARBON DIOXIDE
- METHANE
- HYDROGEN

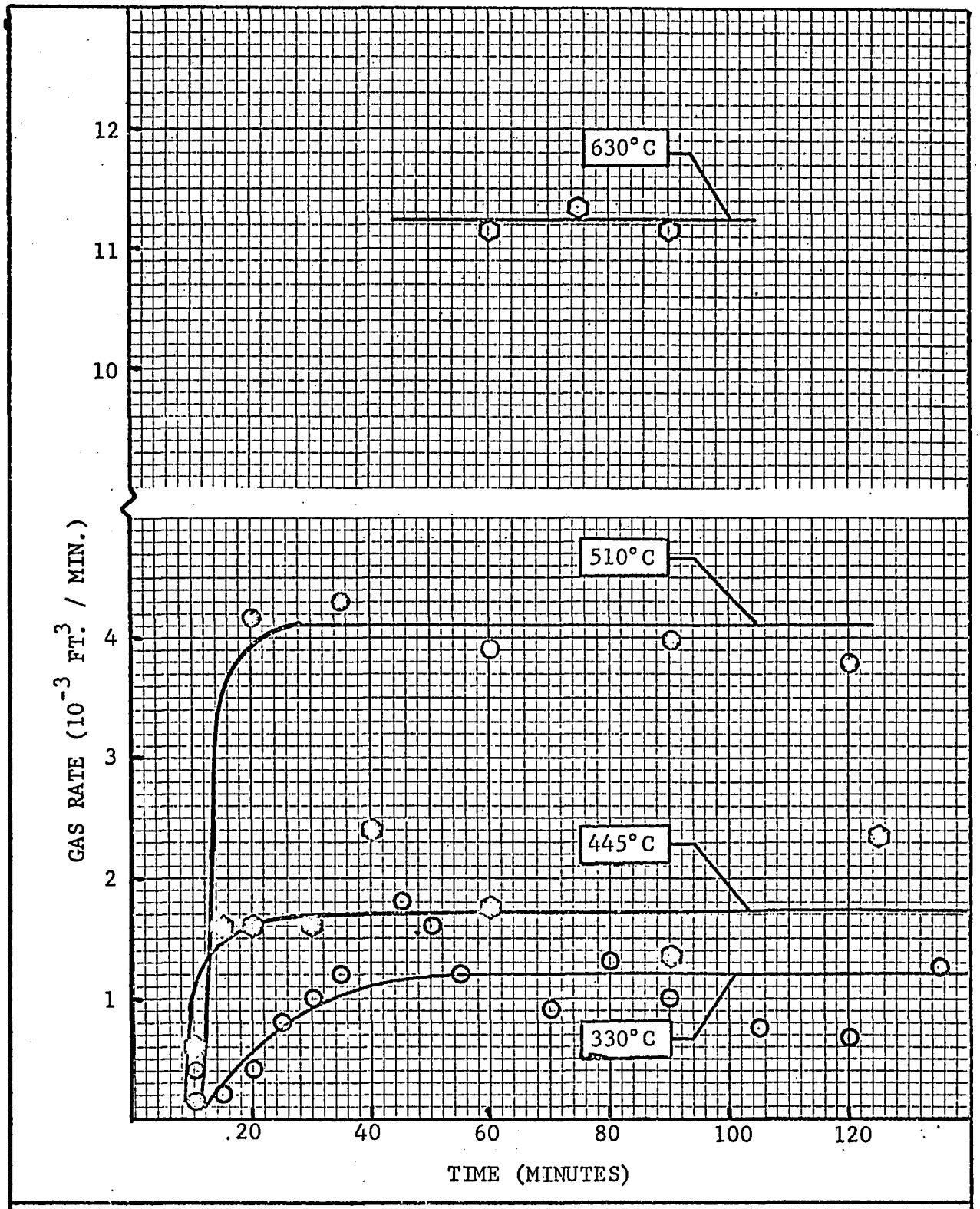

FIGURE III - 21

GAS RATE AS A FUNCTION OF TIME FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED.

- 630°C
- 510°C
- 445°C
- 330°C

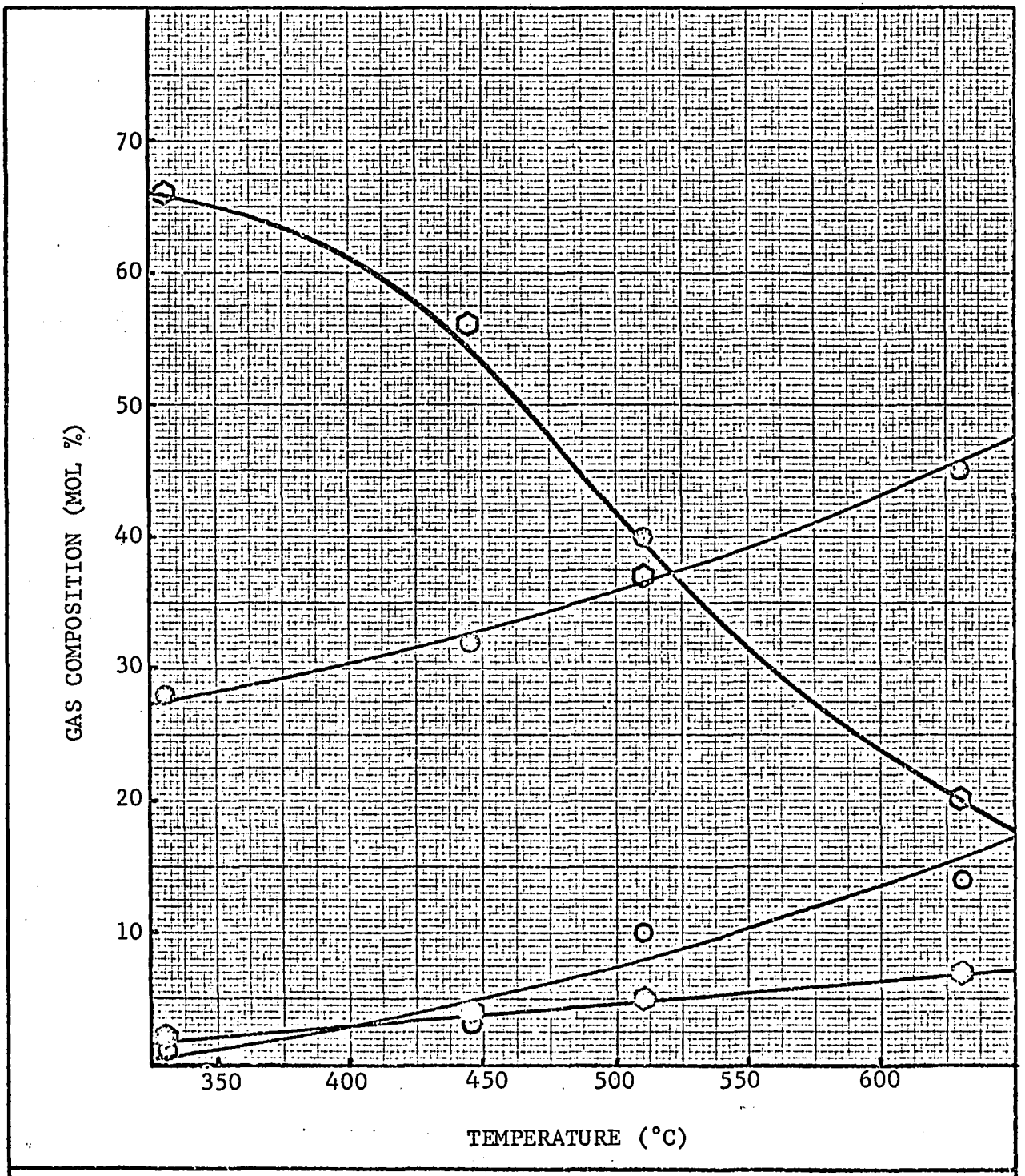

FIGURE III - 22

STEADY STATE GAS COMPOSITION AS A FUNCTION OF TEMPERATURE FOR THE CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED.

- CARBON DIOXIDE
- CARBON MONOXIDE
- HYDROGEN
- METHANE

TABLE III - 2

STEADY STATE COMPOSITION OF OVERHEAD GAS
FROM CONTINUOUS PYROLYSIS OF BAGASSE PITH

REACTION TEMPERATURE (°C)	MOL PER CENT			
	CO	CO_2	CH_4	H_2
330	28	66	1	2
445	32	56	3	4
510	40	37	10	5
630	45	20	14	7

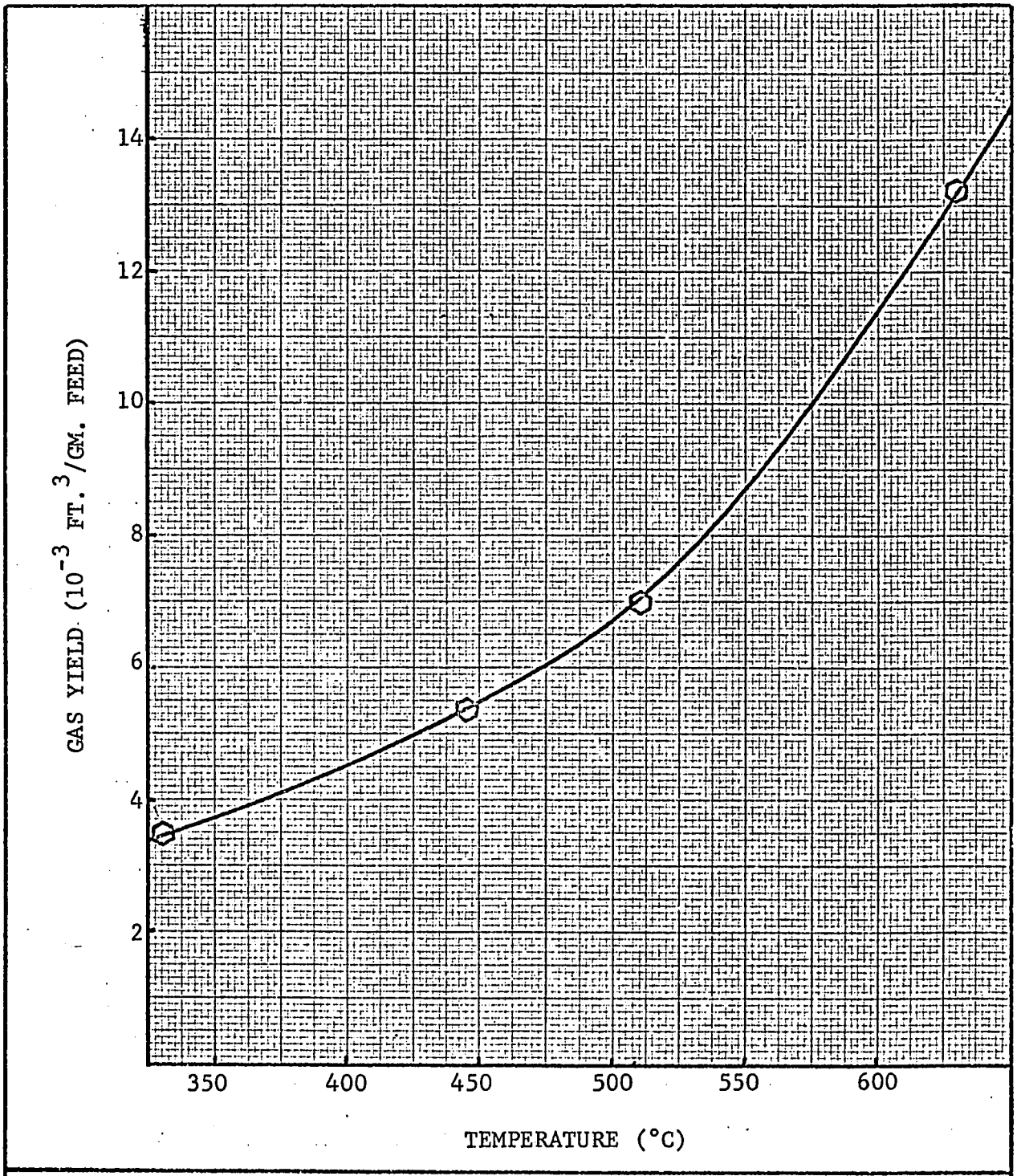

FIGURE III - 23

STEADY STATE GAS YIELD AS A FUNCTION OF TEMPERATURE FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED.

TABLE III - 3

PRODUCT YIELD DATA FOR THE CONTINUOUS PYROLYSIS OF BAGASSE PITH WITH NO STEAM FEED

REACTION TEMPERATURE (°C)	GAS YIELD(1)	TOTAL LIQUID YIELD(2)	SOLID RESIDUE YIELD(3)	ACETIC ACID YIELD(4)	CONCENTRATION OF ACETIC ACID IN OVERHEAD LIQUID(5)
330	3.45×10^{-3}	0.322	0.480	2.15	7.0
445	5.35×10^{-3}	0.362	0.318	3.07	8.5
510	6.99×10^{-3}	0.308	0.313	2.99	9.7
630	13.2×10^{-3}	0.243	0.266	*	*
450(6)	*	*	*	*	8.6

* DATA NOT OBTAINED

(1) $FT.^3/GM.$ OF FEED

(2) GM./GM. OF FEED

(3) GM./GM. OF FEED

(4) GM./100 GM. OF FEED

(5) WT. %

(6) THIS RUN WAS TERMINATED BECAUSE OF EQUIPMENT PROBLEMS BEFORE STEADY STATE WAS REACHED.

shows that the continuous reaction yields about one third as much gaseous products as the batch reactions at corresponding temperatures. Comparison of Figure III-24 with Figure III-17 shows that continuous operation yields about 40% more solid residue than does batch operation at the same temperature. Figure III-25 shows that a maximum in the yield of total liquid products occurs in the temperature range of 350-550°C.

The liquid overhead samples were analized using a gas chromatograph as described in the Experimental Section. The major component was found to be water (about 80-90 wt. %) with acetic acid being present in the next greatest quantity (about 7-10%). A wide range of other products was observed. Some of those identified by retention time were formic acid, formaldehyde and methanol. Identification of the remaining components was not attempted. Figure III-26 and Table III-3 shows the effect of reaction temperature on the acetic acid content of the overhead liquid. The acetic acid yields were found to be 2.2% at 330°C, 3.1% at 445°C and 3.0% at 510°C.

Lignin was observed in the overhead from all of the pyrolysis reactions. The amount observed was greatest for the high temperature runs. It was not possible to get an accurate measure of the amount of this material since it condensed onto the walls of the equipment and, in a short period of time, solidified into an insoluble, black residue. Attempts to prevent this condensation and solidification by heating the walls of the equipment were unsuccessful.

Periodic Acid Cleavage Reaction

Periodic acid (HIO_4) is a very selective oxidizing agent

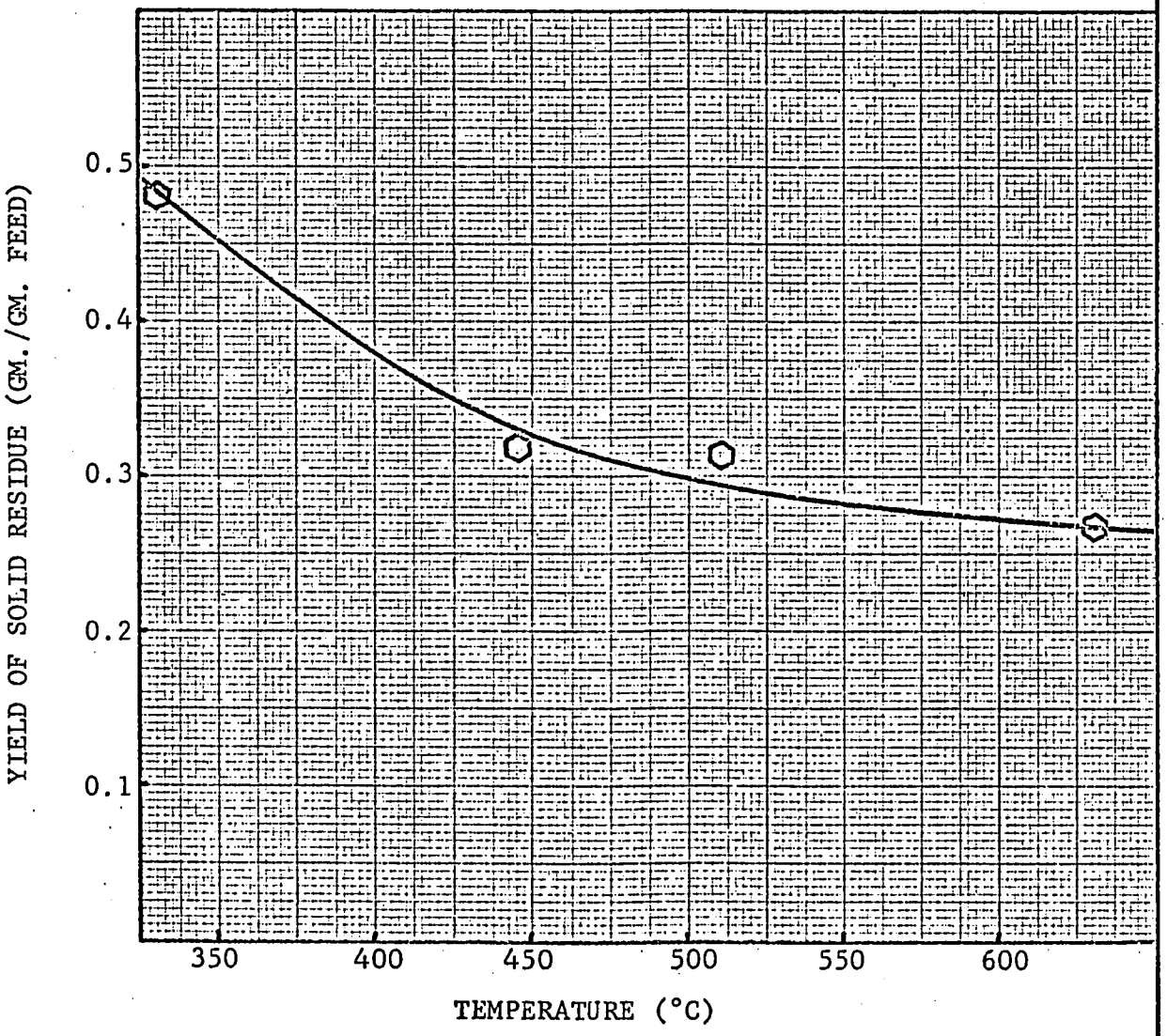

FIGURE III - 24

YIELD OF SOLID RESIDUE AS A FUNCTION OF TEMPERATURE FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED.

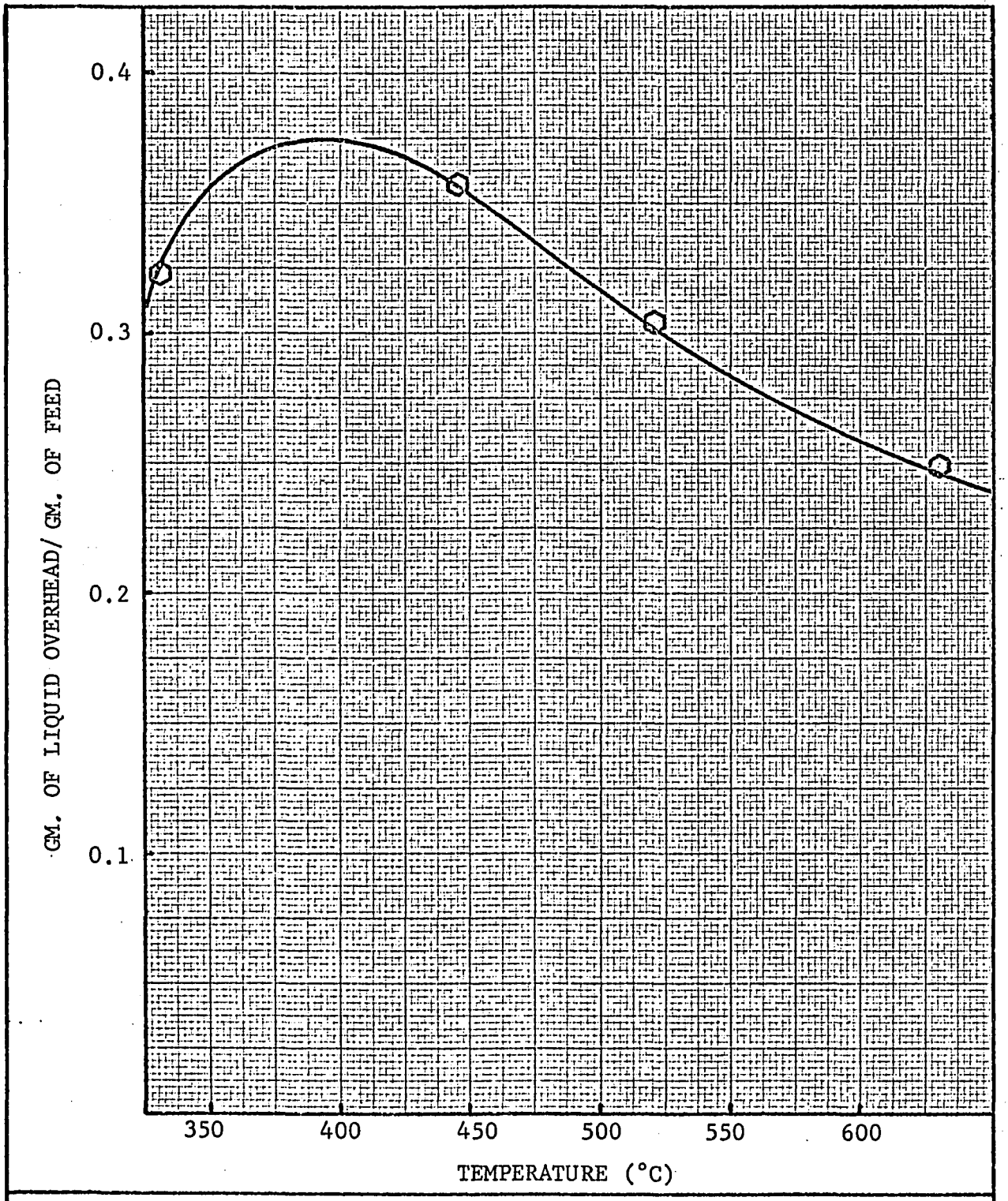

FIGURE III - 25

YIELD OF LIQUID OVERHEAD AS A FUNCTION OF REACTION TEMPERATURE FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED.

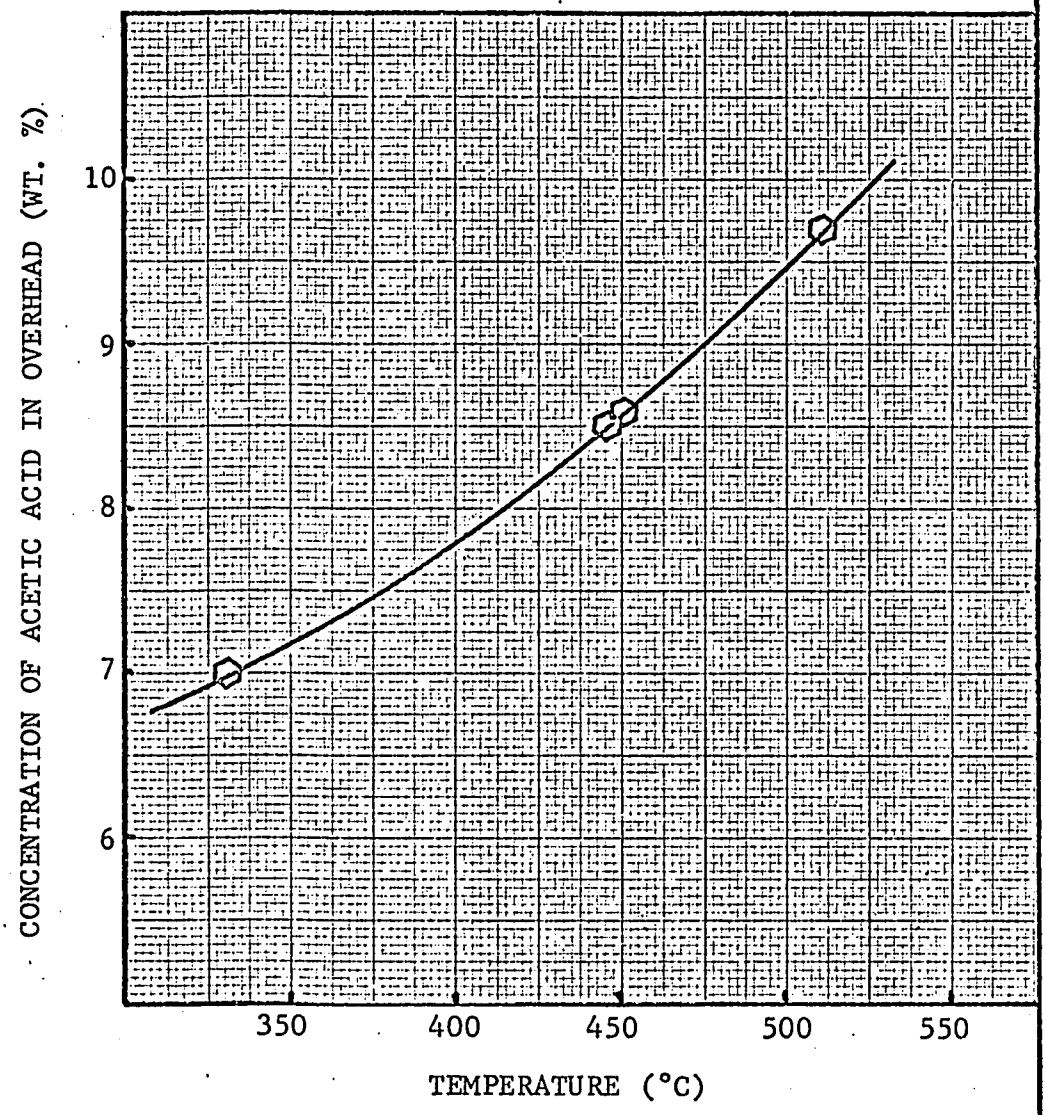

FIGURE III - 26

STEADY STATE CONCENTRATION OF ACETIC ACID IN LIQUID OVERHEAD AS A FUNCTION OF TEMPERATURE FOR THE CONTINUOUS PYROLYSIS OF BAGASSE PITH WITHOUT STEAM FEED.

which will cleave the C-C bond of a vicinal diol(3). When reacted with cellulose, cleavage of the 2,3 C-C bond of the cellulose mesomer unit and oxidation of each of these carbon atoms to the aldehyde results as described in Chapter I and as illustrated in Figure I-4. The high selectivity of this reaction made it useful as a method of increasing the intramolecular mobility by cleavage of the bond between the vicinal diols.

All cleavage reactions were run batchwise at room temperature with no provisions for temperature control. Filter paper was used as the feed material for these reactions since the major purpose of this work was to test the proposed theory of activation. It was felt that impurities in the by-product cellulosics might mask the effects of the HIO_4 reaction.

Samples of the reaction mixture were removed periodically and analized for HIO_4 content as described in Chapter II. The amount of periodic acid that had reacted was calculated by multiplying the change in HIO_4 concentration (gm. mols/liter) by the volume of acid solution fed to the reactor. The initial concentration of cellulose was calculated by dividing the weight of cellulose fed (grams) by 162, the molecular weight of a cellulose monomer unit. This number was then divided by the volume of acid solution fed to the reactor to obtain the initial concentration of cellulose (gm. mols/liter). Subsequent cellulose concentrations were calculated by substracting the change in concentration of the HIO_4 from the initial concentration of the cellulose. This of course assumes 100% yield based on the HIO_4.

It was assumed that the reaction would be first order with respect to the HIO_4 and to the cellulose giving an overall reaction order of two. Such a reaction would obey the rate equation:

$$-\frac{dC_A}{dt} = k\,C_A C_B \qquad (1)$$

where C_A = concentration of component A (mols/liter)

C_B = concentration of component B (mols/liter)

k = reaction rate constant (liters/(mol.)(minute))

t = time (minutes)

The fraction reacted, X, is defined by the equation:

$$X = \frac{C_{Ao} - C_A}{C_{Ao}} \qquad (2)$$

where C_{Ao} = initial concentration of component A

If the stoichiometry of the reaction is represented by the equation A + B $\longrightarrow$ products a relation between C_A and C_B can be established:

$$C_B = C_{Bo} - XC_{Ao} \qquad (3)$$

Finally defining $M = C_{Bo}/C_{Ao}$ and substituting into equation (1) yields:

$$-C_{Ao}\frac{d(1-X)}{dt} = k\,C_{Ao}^2\,(1-X)\,(M-X)$$

$$\frac{dX}{dt} = k\,C_{Ao}\,(1-X)\,(M-X)$$

$$\frac{dX}{(1-X)(M-X)} = k\,C_{Ao}\,dt \qquad (4)$$

Integrating equation (4) from X = 0 at time t = 0 to X = X at time = t yields:

$$\ln \frac{M-X}{M(1-X)} = C_{Ao} (M-1) kt \qquad (5)$$

Substituting back to obtain the equation in the form of concentration units gives:

$$\ln \frac{C_B}{MC_A} = (C_{Bo} - C_{Ao}) kt \qquad (6)$$

or

$$\ln {}^{C_B}/_{C_A} = (C_{Bo} - C_{Ao}) kt + \ln M \qquad (7)$$

Equation (7) says that if $\ln {}^{C_B}/_{C_A}$ is plotted as a function of time a straight line should be obtained with slope equal to $k(C_{Bo}-C_{Ao})$ and its intercept should equal ln M. If experimental data is so plotted and a straight line is obtained, this is taken as proof that the reaction is first order with respect to each component as assumed in the derivation of the equation. Levenspiel (2) points out that in running the experiments it is necessary that the initial reactant concentration ratio, M, not be too close to 1.0 since the integrated rate equation becomes indeterminant at M = 1.0.

Experimental data obtained in this study were plotted in the manner described and straight lines were obtained as shown in Figures III-27 and 28. The experimental data are tabulated in Appendix C. The slope of the line obtained in each experiment was measured and the reaction rate constant was calculated. Table III-4 summarizes

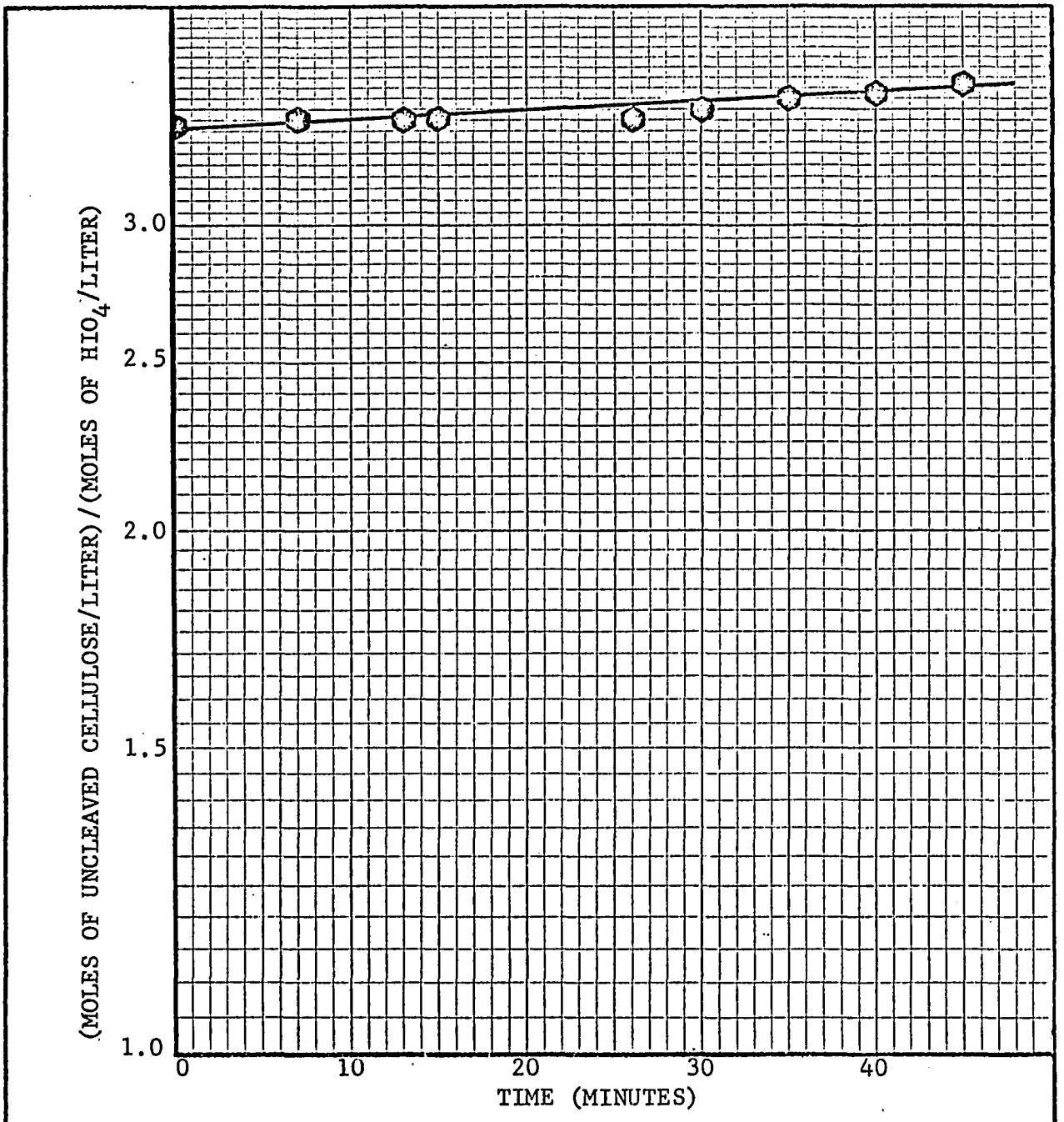

FIGURE III-27

KINETIC DATA FOR DETERMINING THE REACTION RATE CONSTANT FOR CLEAVAGE OF THE 2,3 C-C BONDS IN CELLULOSE BY PERIODIC ACID (HIO_4). THE REACTION TEMPERATURE WAS ABOUT 25°C. INITIAL CONCENTRATION OF HIO_4 WAS 0.130 GM. MOL/LITER. INITIAL CONCENTRATION OF CELLULOSE WAS 0.443 GM. MOL/LITER.

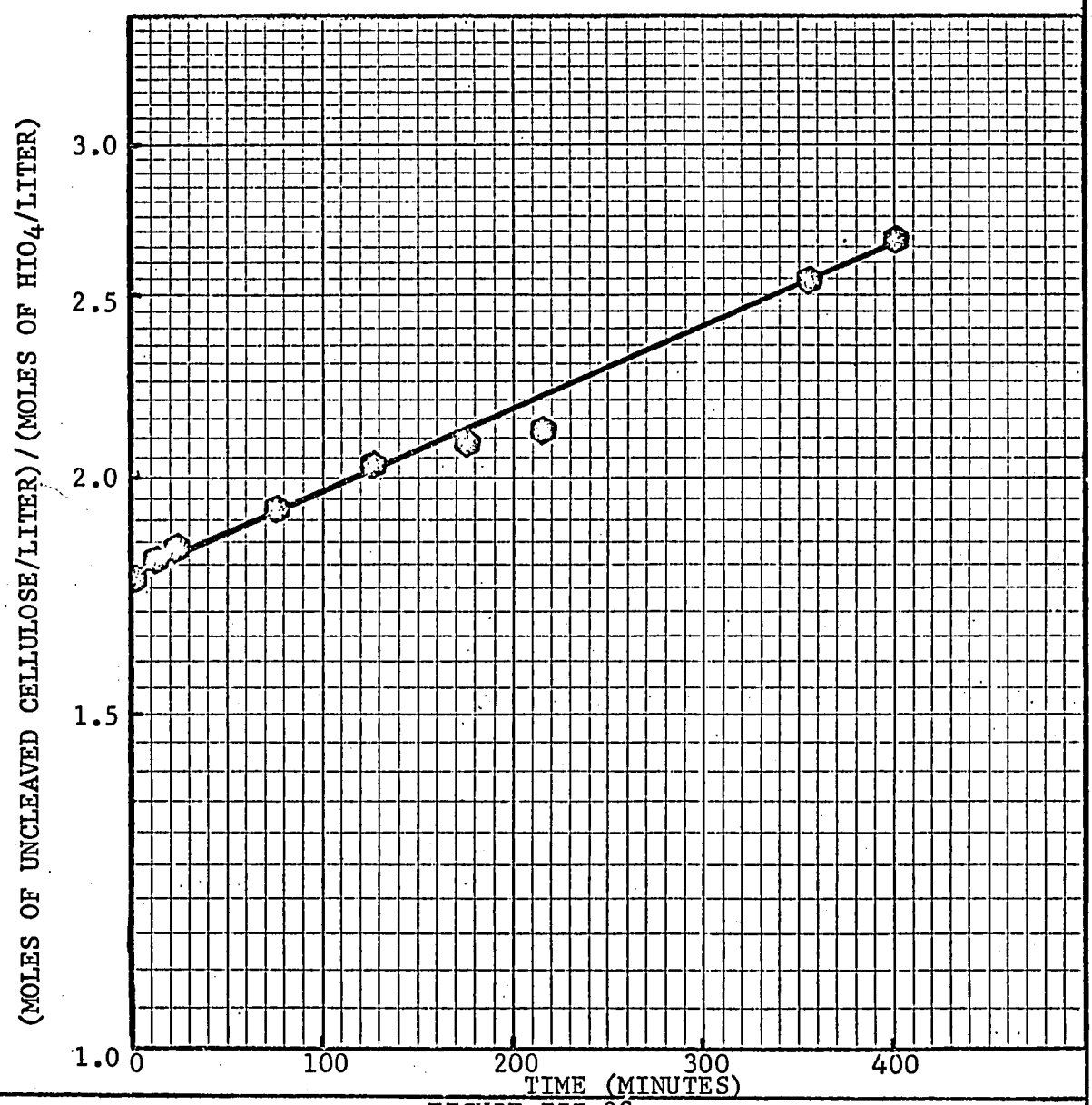

FIGURE III-28

KINETIC DATA FOR DETERMINING THE REACTION RATE CONSTANT FOR THE CLEAVAGE OF THE 2,3 C-C BONDS IN CELLULOSE BY PERIODIC ACID (HIO_4). THE REACTION TEMPERATURE WAS 25° C. INITIAL CONCENTRATION OF HIO_4 = 0.5385 GM. MOLS/LITER. INITIAL CONCENTRATION OF CELLULOSE = 0.960 GM. MOLS/LITER.

TABLE III - 4

EXPERIMENTAL VALUES FOR THE REACTION RATE CONSTANT FOR THE REACTION OF PERIODIC ACID WITH CELLULOSE. ALL REACTIONS WERE RUN AT ROOM TEMPERATURE.

REACTION RATE CONSTANT (LITERS/GM. MOL/MINUTE)	FINAL % REACTED	INITIAL ACID CONCENTRATION (GM. MOL/LITER)	INITIAL CELLULOSE CONCENTRATION (GM. MOL/LITER)
2.63×10^{-3}	2.3	0.130	0.443
3.40×10^{-3}	9.9	0.500	0.617
1.65×10^{-3}	19.6	0.585	0.536
2.40×10^{-3}	29.6	0.536	0.960

AVERAGE

2.52×10^{-3}

the rate data that were obtained. The rate constant was found to vary from 1.65×10^{-3} to 3.40×10^{-3} with an average value of 2.52×10^{-3} (liters/(gm. mol)(min.)). The variation in the values can be attributes to the lack of temperature control and to the difficulties in obtaining a good sample of the reaction mixture as described in Chapter II.

Carbonization and Activation Reactions

The cellulose that had been reacted with periodic acid was washed, filtered and then dried under vacuum. This dried material was then fed to the carbonization reactor as described in Chapter II. The reactor was placed in a muffle furnace at 450°C for about 24 hours. The weight of the feed material and the residue was recorded and the per cent weight loss (burnoff) was calculated. Figure III-29 shows that the burnoff decreases as the amount of cleavage increases. The data are tabulated in Table III-5. These data indicated that cleavage of some of the 2,3 C-C bonds in the cellulose causes a change in the mechanism during carbonization. This effect appears to increase with increased cleavage of the 2,3 C-C bonds up to about 15%. At higher cleavages the effect of the cleavage treatment on burnoff during carbonization appears to change very little.

As stated in Chapter I activation of the carbonized cellulose is accomplished by reacting it with an oxidizing medium. Steam, air and carbon dioxide as single feeds or as mixtures are used for activating the chars. In this study carbon dioxide was chosen as the oxidizing medium. All runs were made at the same temperature (800-850°C) and using the same carbon dioxide feed rate (0.0065 ft^3/min) as described in Chapter II.

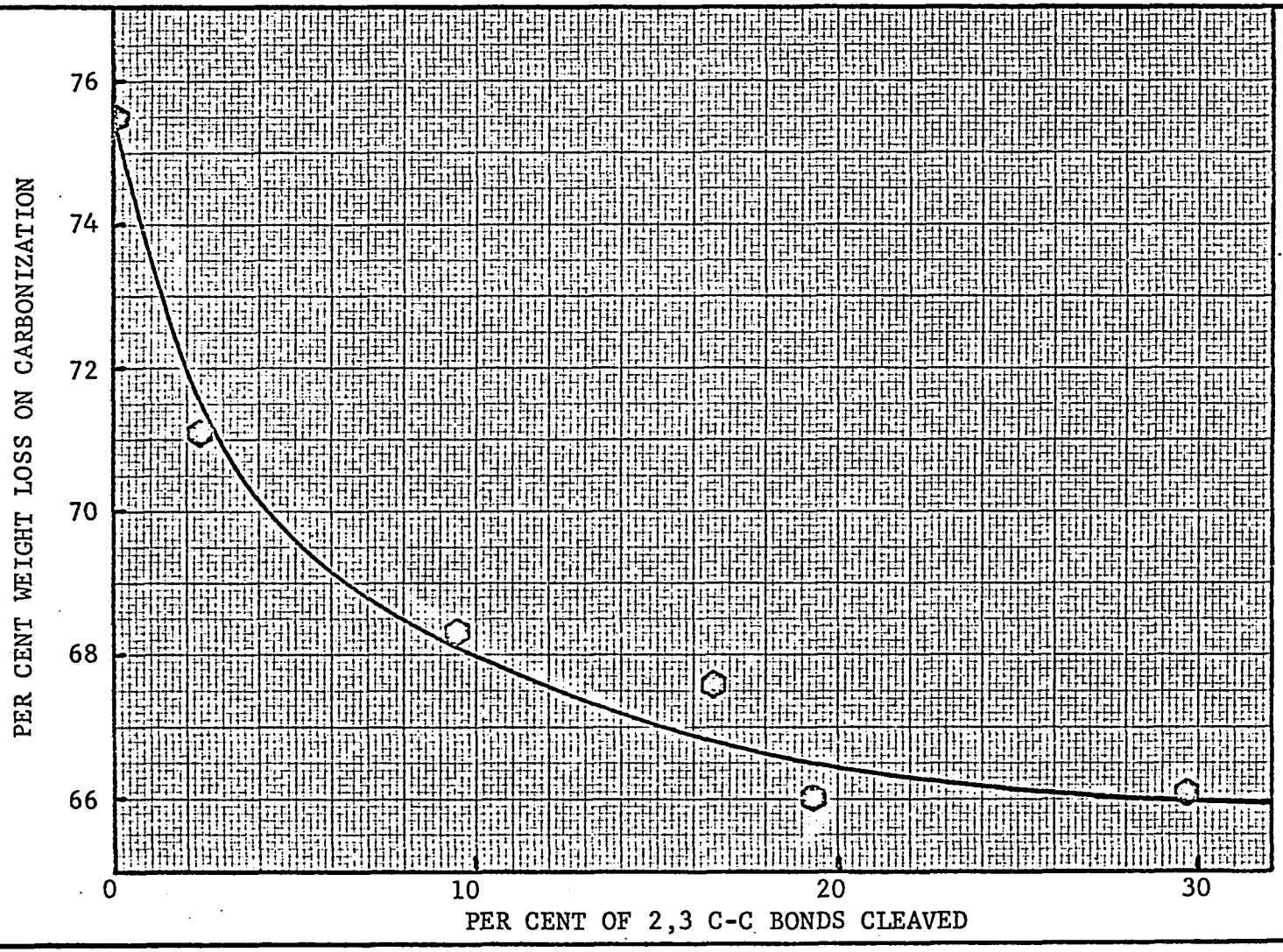

FIGURE III - 29

PER CENT WEIGHT LOSS ON CARBONIZATION FOR 24 HOURS AT 450°C AS A FUNCTION OF THE PER CENT OF THE 2,3 C-C BONDS CLEAVED FOR CELLULOSE THAT HAS BEEN REACTED WITH PERIODIC ACID.

TABLE III - 5

DATA FOR THE BURNOFF DURING CARBONIZATION AND ACTIVATION FOR CELLULOSE IN WHICH THE 2,3 C-C BONDS WERE CLEAVED WITH PERIODIC ACID PRIOR TO CARBONIZATION

% OF 2,3 C-C BONDS CLEAVED IN ORIGINAL CELLULOSE	BURNOFF DURING CARBONIZATION (%)	ACTIVATION TIME (MINUTES)	BURNOFF DURING ACTIVATION (%)	TOTAL BURNOFF (%)
0	75.5	720	34.7	83.9
0	75.5	755	54.6	88.9
0	75.5	1080	61.7	90.6
2.3	71.1	390	28.9	79.5
2.3	71.1	510	31.7	80.3
2.3	71.1	720	56.6	87.4
9.9	68.7	480	36.0	79.9
9.9	68.7	900	38.9	80.9
9.9	68.7	1080	48.4	83.8
9.9	68.7	1440	55.3	86.0
16.5	67.6	1080	69.0	88.8
19.2	66.0	480	32.1	76.9
19.2	66.0	780	32.5	77.1
19.2	66.0	1065	49.6	82.9
29.6	66.2	480	32.0	77.0
29.6	66.2	725	47.5	82.3
29.6	66.2	1115	56.0	85.2

The char was weighed before and after activation and the burnoff was calculated. These data are shown graphically as a function of the residence time in the activation reactor in Figure III-30 and are tabulated in Table III-5. The total burnoff based on the cleaved cellulose was calculated by combining the burnoff during carbonization and the burnoff during activation. These data are also tabulated in Table III-5 and are shown graphically in Figure III-31.

The fact that the burnoff during carbonization decreases with increasing cleavage suggests that oxidation of the number 2 and 3 carbon atoms from the alcohol to the aldehyde state inhibits the carbonization reaction at a temperature of 450°C. This inhibition is not noticed, however, at the higher activation temperature (800-850°C). This implies that the mechanism of carbonization has been changed by first reacting the uncarbonized cellulose with periodic acid. This is what our proposed theory for the production of activated carbon had predicted.

Evaluation of Activated Carbon

As stated in Chapter I the method used to evaluate the relative activity of the carbons used in this study was the adsorption of methylene blue from water solutions. Kipling and Wilson (4) have investigated the use of this method for the determination of surface areas. They conclude that the method can be used as a semi-quantitative molecular probe but that more needs to be known about its adsorption before it can be used reliably for quantative estimations of surface areas. They point out, however, that the method is used for routine comparative work. Gleysteen and Scheffler (5) have pointed out that, while this type of standardized test is widely used as a

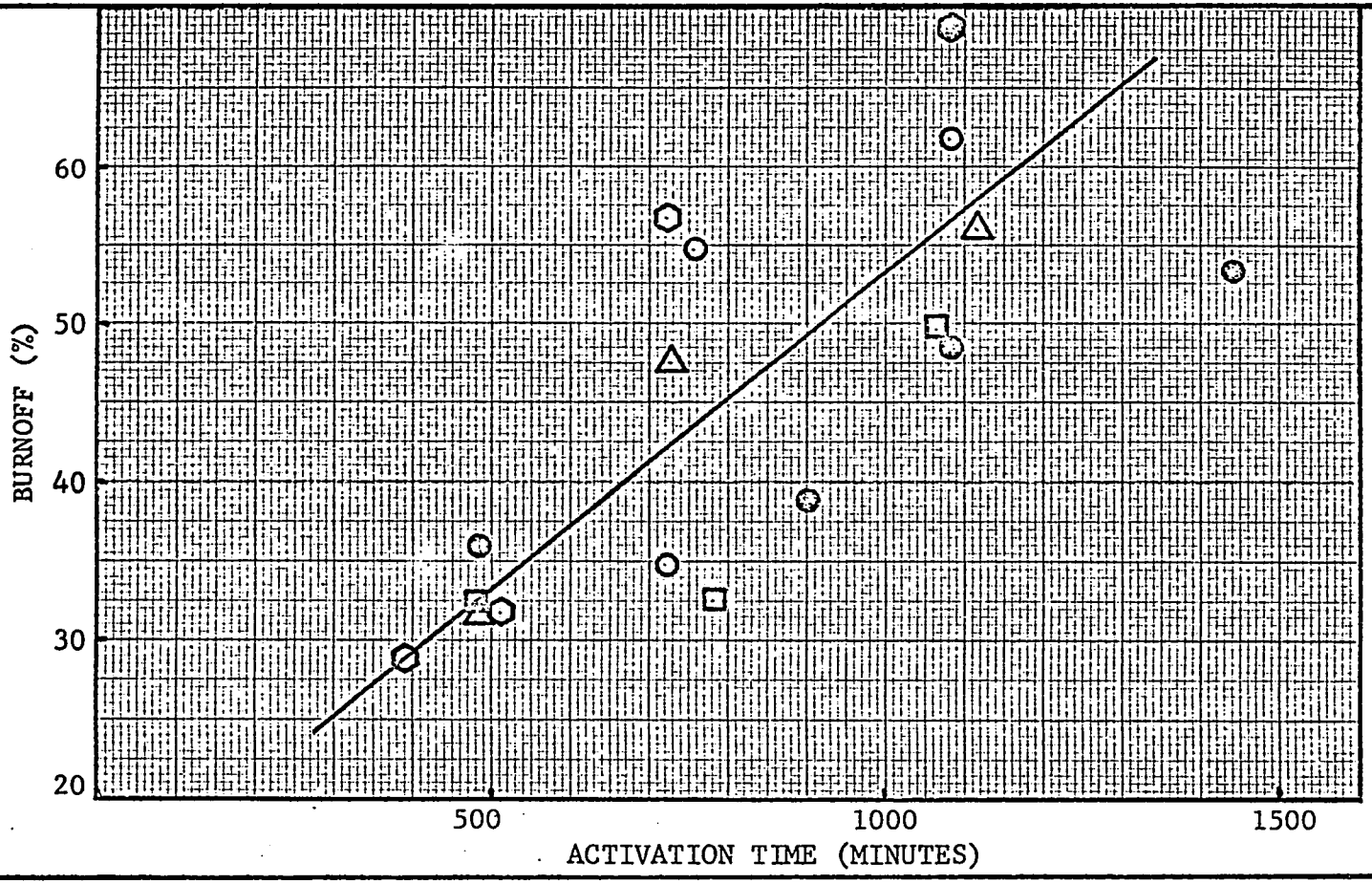

FIGURE III - 30

BURNOFF DURING ACTIVATION AS A FUNCTION OF RESIDENCE TIME IN ACTIVATION REACTOR FOR CHARS MADE FROM CELLULOSE IN WHICH THE 2,3 C-C BONDS WERE CLEAVED WITH HIO_4 BEFORE CARBONIZATION.

- 0% OF 2,3 C-C BONDS CLEAVED
- 2.3% OF 2,3 C-C BONDS CLEAVED
- 9.4% OF 2,3 C-C BONDS CLEAVED
- 16.5% OF 2,3 C-C BONDS CLEAVED
- 19.2% OF 2,3 C-C BONDS CLEAVED
- 29.6% OF 2,3 C-C BONDS CLEAVED

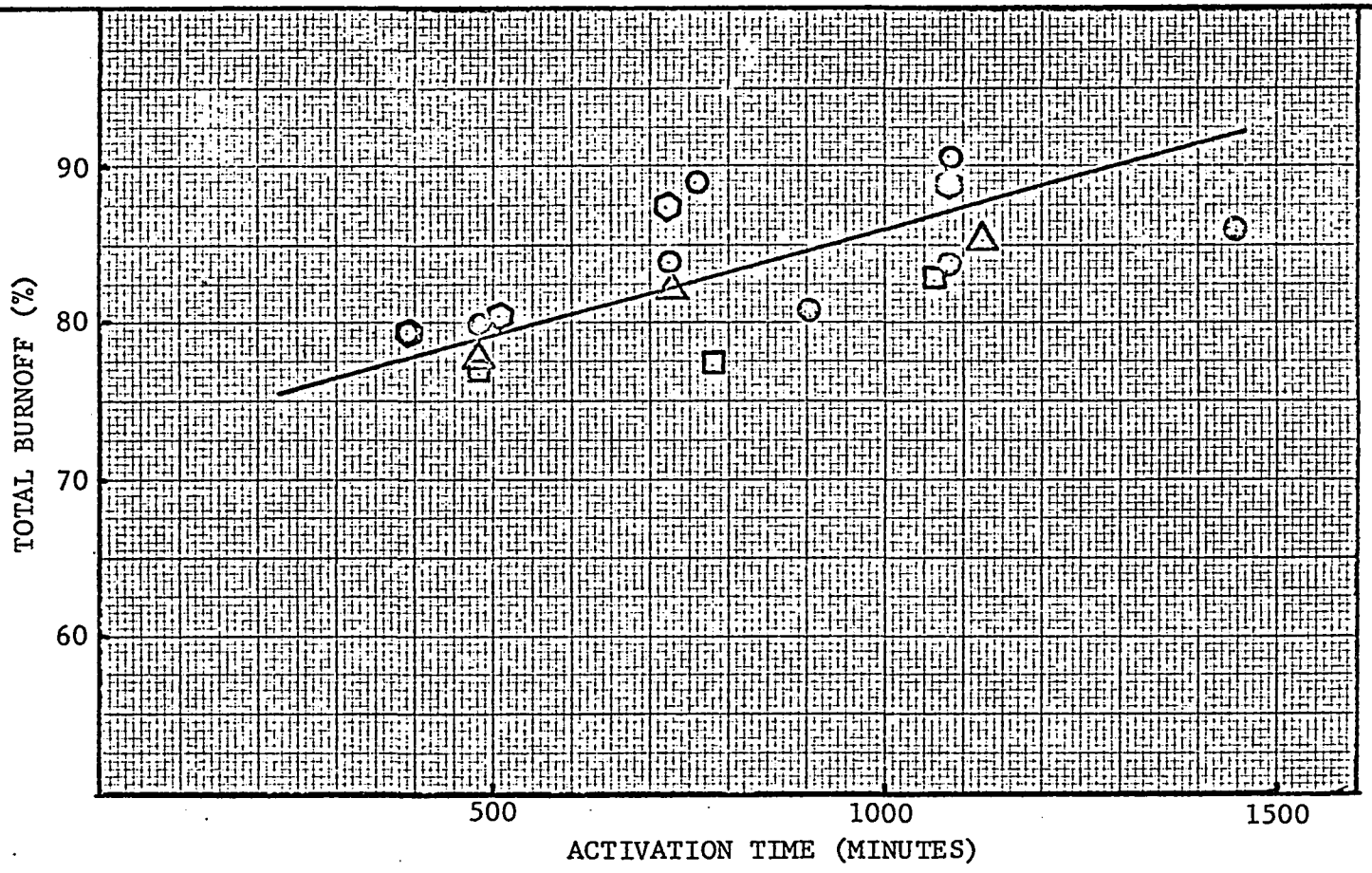

FIGURE III - 31

TOTAL BURNOFF (CARBONIZATION PLUS ACTIVATION) FOR CELLULOSE IN WHICH THE 2,3 C-C BONDS HAVE BEEN CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION AS A FUNCTION OF ACTIVATION TIME.

○ 0% OF 2,3 C-C BONDS CLEAVED
⬡ 2.3% OF 2,3 C-C BONDS CLEAVED
⊙ 9.4% OF 2,3 C-C BONDS CLEAVED
⬡ 16.5% OF 2,3 C-C BONDS CLEAVED
□ 19.2% OF 2,3 C-C BONDS CLEAVED
△ 29.6% OF 2,3 C-C BONDS CLEAVED

basis for comparing activated carbons, there is not necessarily a very good correlation between the performance of a carbon in one of these tests and its performance in some slightly different field of application. Consequently, it must be emphasized that the only way to select a carbon for a particular application is to test the carbon under the conditions for which it is to be used.

Kipling (6) discusses a variety of equations for fitting adsorption isotherms. The most popular of these appears to be the Freundlich equation:

$$\frac{X}{M} = AC^{1/n} \qquad (8)$$

Where X = amount of material adsorbed on M weight of solid at an equilibrium concentration of C; A and n are constants. The form 1/n is used to emphasize that C is raised to a power less than unity. This equation works very well in fitting adsorption data of the form shown in Figure III-32. This is typical of the form of the methylene blue adsorption isotherm.

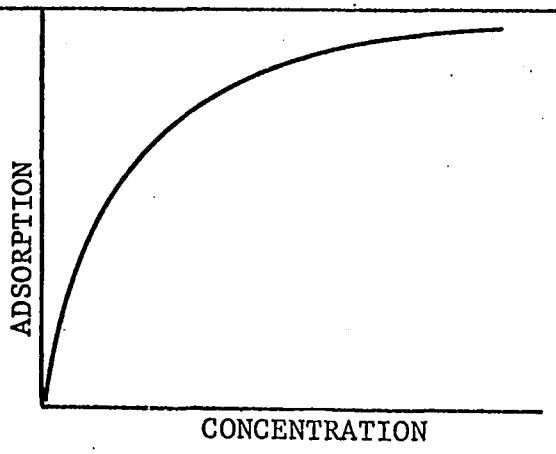

FIGURE III - 32

ADSORPTION ISOTHERM FOR WHICH FREUNDLICH EQUATION IS APPLICABLE.

Equation (8) can be linerized by taking logarithms of both sides to give:

$$\log \frac{X}{M} = \log A + \frac{1}{n} \log C \qquad (9)$$

This equation shows that a plot of $\log \frac{X}{M}$ vs log C should give a straight line of slope 1/n.

The value $\frac{X}{M}$ is a measure of the adsorptive capacity of the solid being investigated. Equation (8) indicates that this adsorptive capacity is a function of the equilibrium concentration of the resulting solution. Therefore, if the adsorptive capacity of different adsorbing solids is to be compared it is necessary that the comparison be done at the same concentration. Fuchs (7) has shown that the pH and temperature must be the same also.

The usual method for utilizing the Freundlich plots is to establish a standard carbon against which all other carbons are compared. The relative adsorptive power, γ, is defined by the equation:

$$\gamma = \left[\frac{\left(\frac{X}{M}\right)}{\left(\frac{X}{M}\right)_S} \right]_{C,pH,T}$$

where $\left(\frac{X}{M}\right)$ = adsorptive power of carbon being evaluated

$\left(\frac{X}{M}\right)_S$ = adsorptive power of standard carbon

The subscripts C, pH, and T are used to denote that the adsorptive capacities must be measured at the same equilibrium concentratin, pH,

and temperature.

In this study a standard solution of methylene blue was made up to be used in obtaining all of the adsorption data. The adsorption data were plotted on log-log graph paper to yield a Freundlich type adsorption isotherm. These isotherms were extrapolated to the initial solution concentration and the value of $\frac{X}{M}$ corresponding to this concentration was read from the graph. The adsorption isotherm for a commercial activated vegetable char, Nuchar B-100-N, was obtained and is given in Figure III-32 (all adsorption experimental data are tabulated in Appendix D). The adsorptive capacity of this carbon at the initial solution concentration (2500ppm) was read from the graph as 270 (mg. methylene blue adsorbed/gm. of carbon). This value was then used as $\left(\frac{X}{M}\right)_S$ and all carbons prepared in this study were evaluated by comparison with this standard using the defined relative adsorptive capacity, γ.

The adsorption data for the activated carbons made in this study are plotted in the Freundlich fashion in Figures III-33-39, the data are tabulated in Appendix D. The extrapolated value of the adsorptive capacity, $\frac{X}{M}$, was obtained from these figures and the relative adsorptive capacity was calculated. These values are tabulated in Table III-6 and are shown graphically in Figure III-40. These data show that the adsorptive capacity increases very rapidly with increasing burnoff up to a total burnoff of about 82-84% at which point the adsorptive capacity appears to increase very little with increasing burnoff.

Figure III-40 shows that there is very little difference in the adsorptive capacity of the carbons prepared from cellulose in

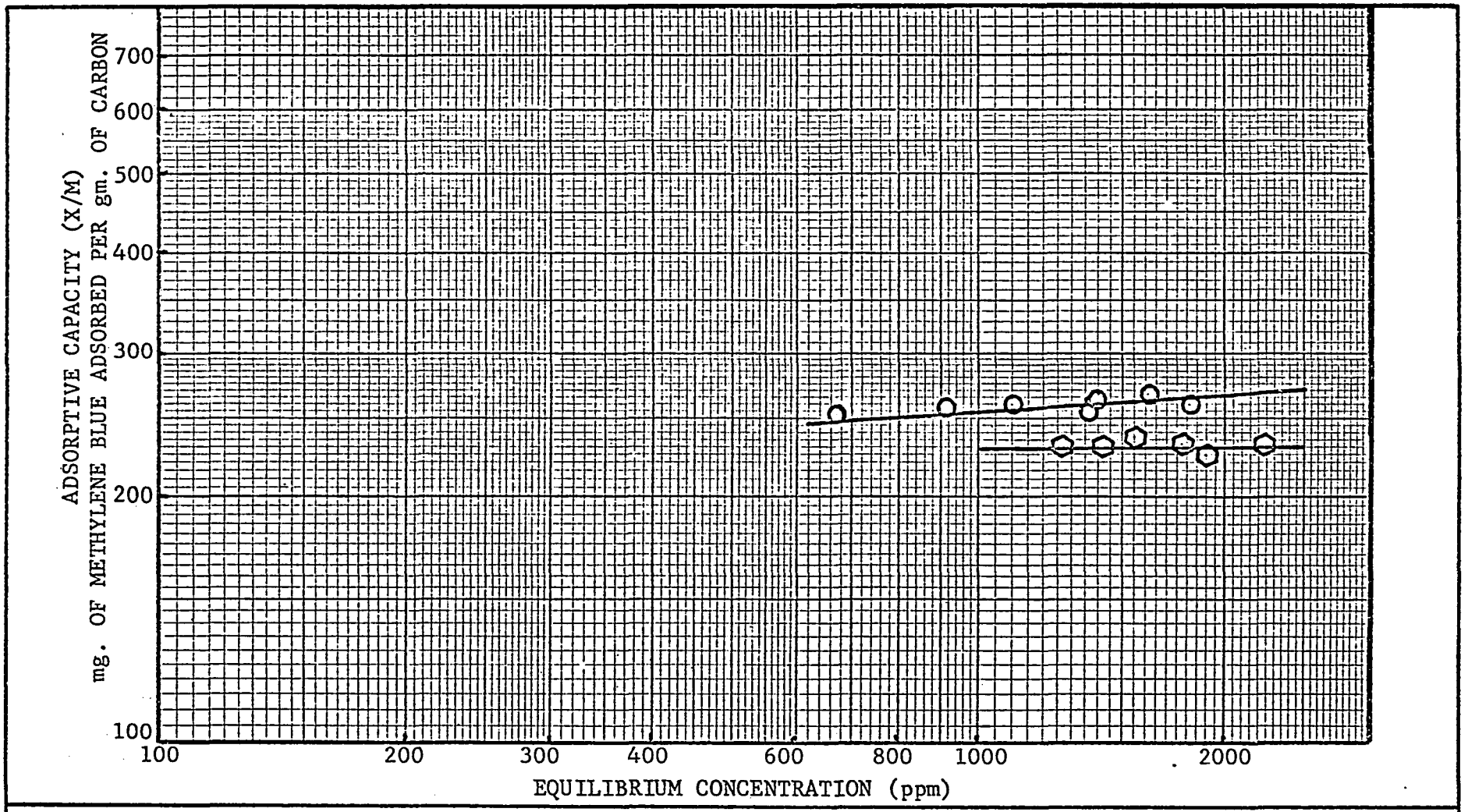

FIGURE III - 33

FREUNDLICH TYPE PLOT FOR THE ADSORPTION OF METHYLENE BLUE FROM WATER USING COMMERCIAL ACTIVATED CARBONS MADE FROM VEGETABLE CHARS.

○ NUCHAR B-100-N

⬡ NUCHAR AQUA A

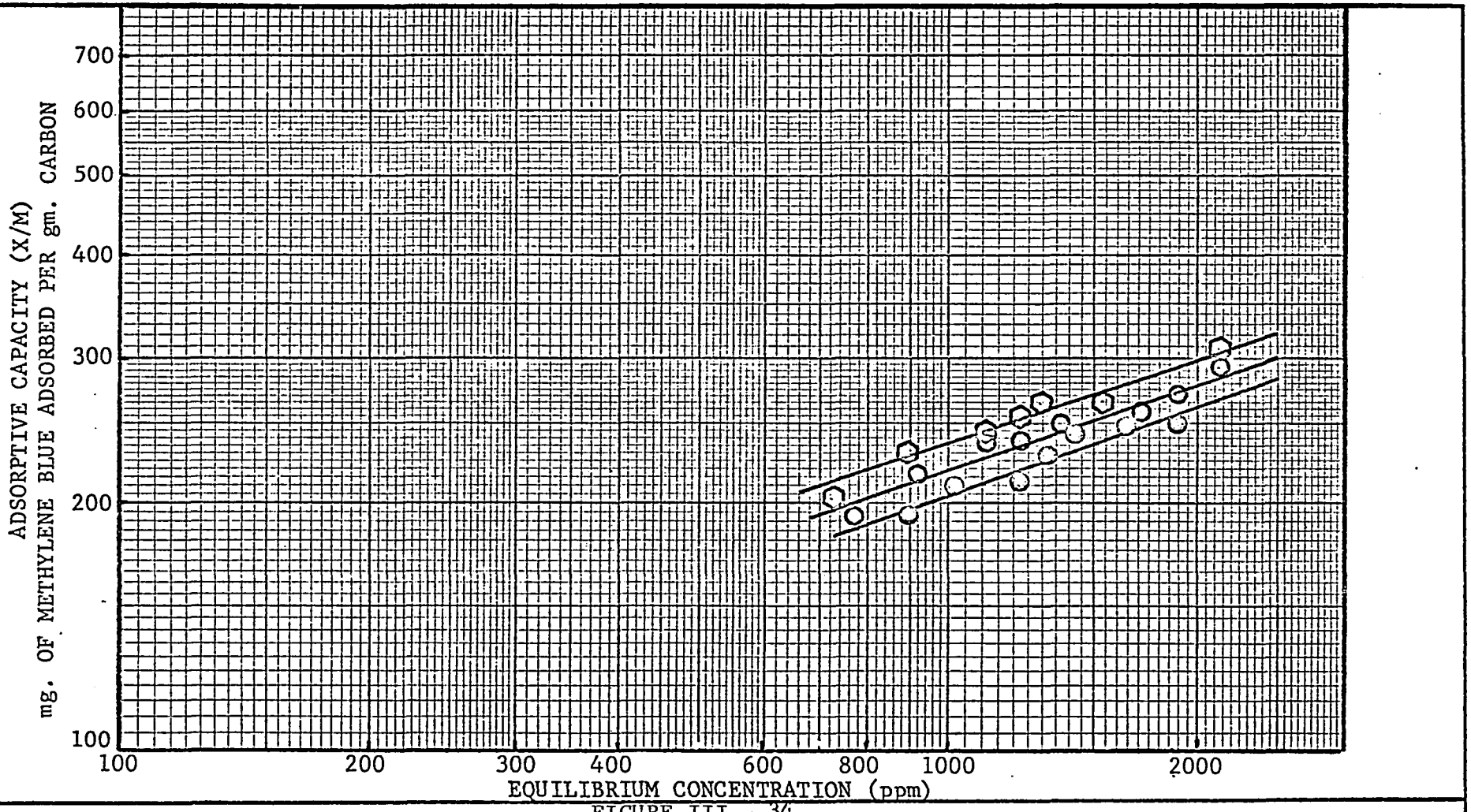

FIGURE III - 34

FREUNDLICH TYPE PLOT FOR THE ADSORPTION OF METHYLENE BLUE FROM WATER USING ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH NONE OF THE 2,3 C-C BONDS WERE CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION.

- ○ 83.9% TOTAL BURNOFF
- ⬡ 88.9% TOTAL BURNOFF
- ○ 90.6% TOTAL BURNOFF

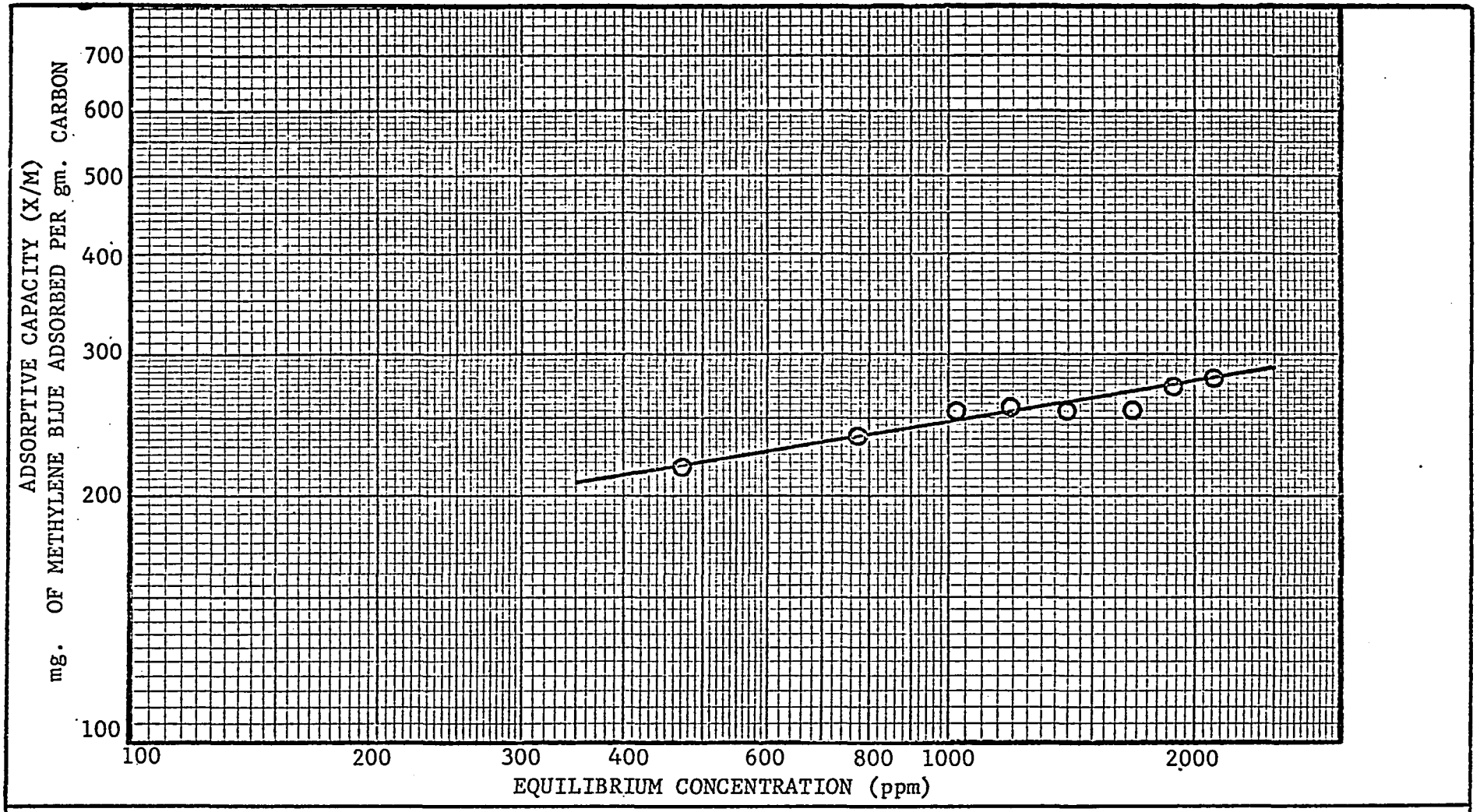

FIGURE III - 35

FREUNDLICH TYPE PLOT OF METHYLENE BLUE ADSORPTION ISOTHERMS FOR ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH <1.0% OF THE 2,3 C-C BONDS WERE CLEAVED BEFORE CARBONIZATION

O 90% TOTAL BURNOFF

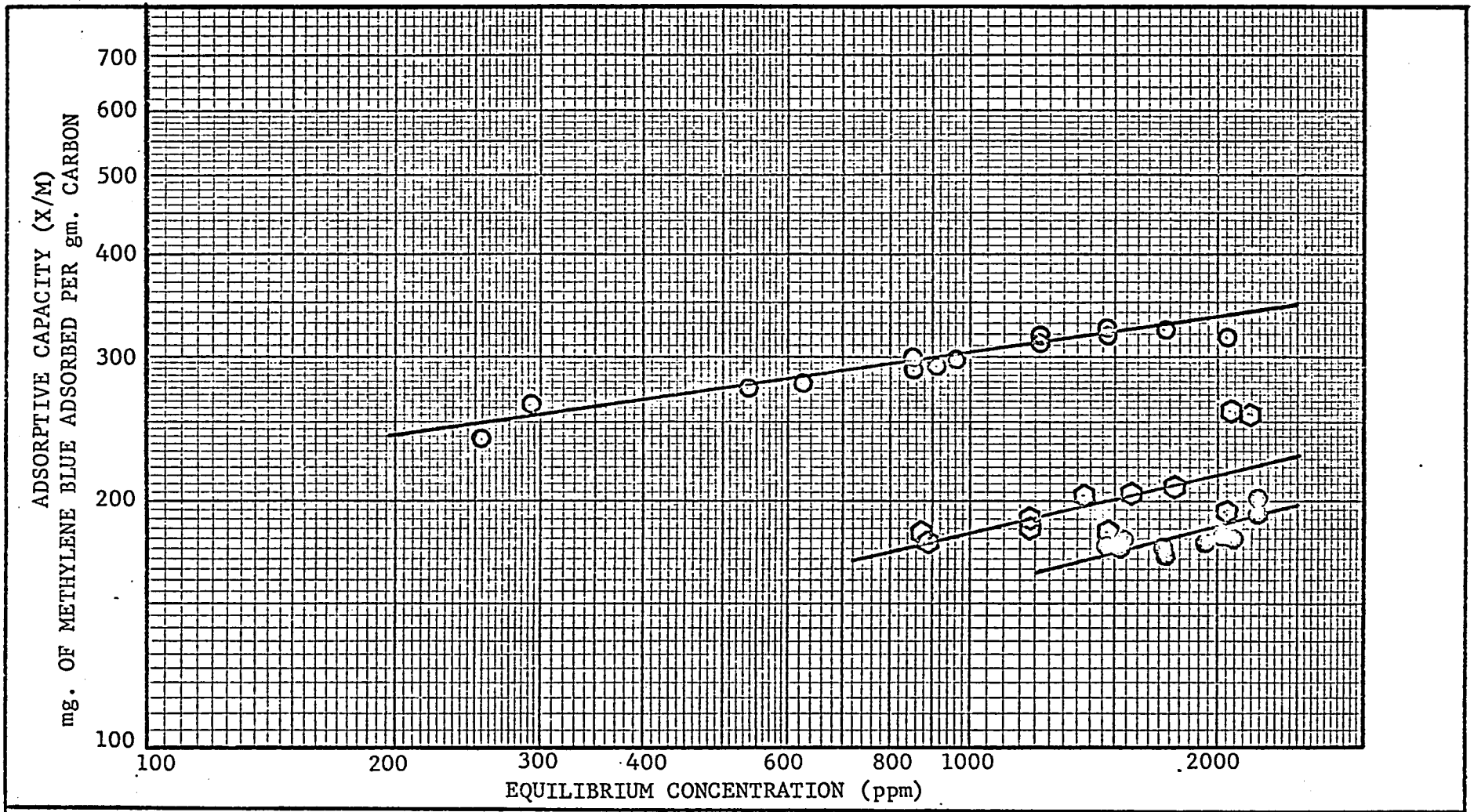

FIGURE III-36

FREUNDLICH TYPE PLOT OF METHYLENE BLUE ADSORPTION ISOTHERMS FOR ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 2.3% OF THE 2,3 C-C BONDS WERE CLEAVED BEFORE CARBONIZATION

○ 87.4% TOTAL BURNOFF
⬡ 80.3% TOTAL BURNOFF
◎ 79.5% TOTAL BURNOFF

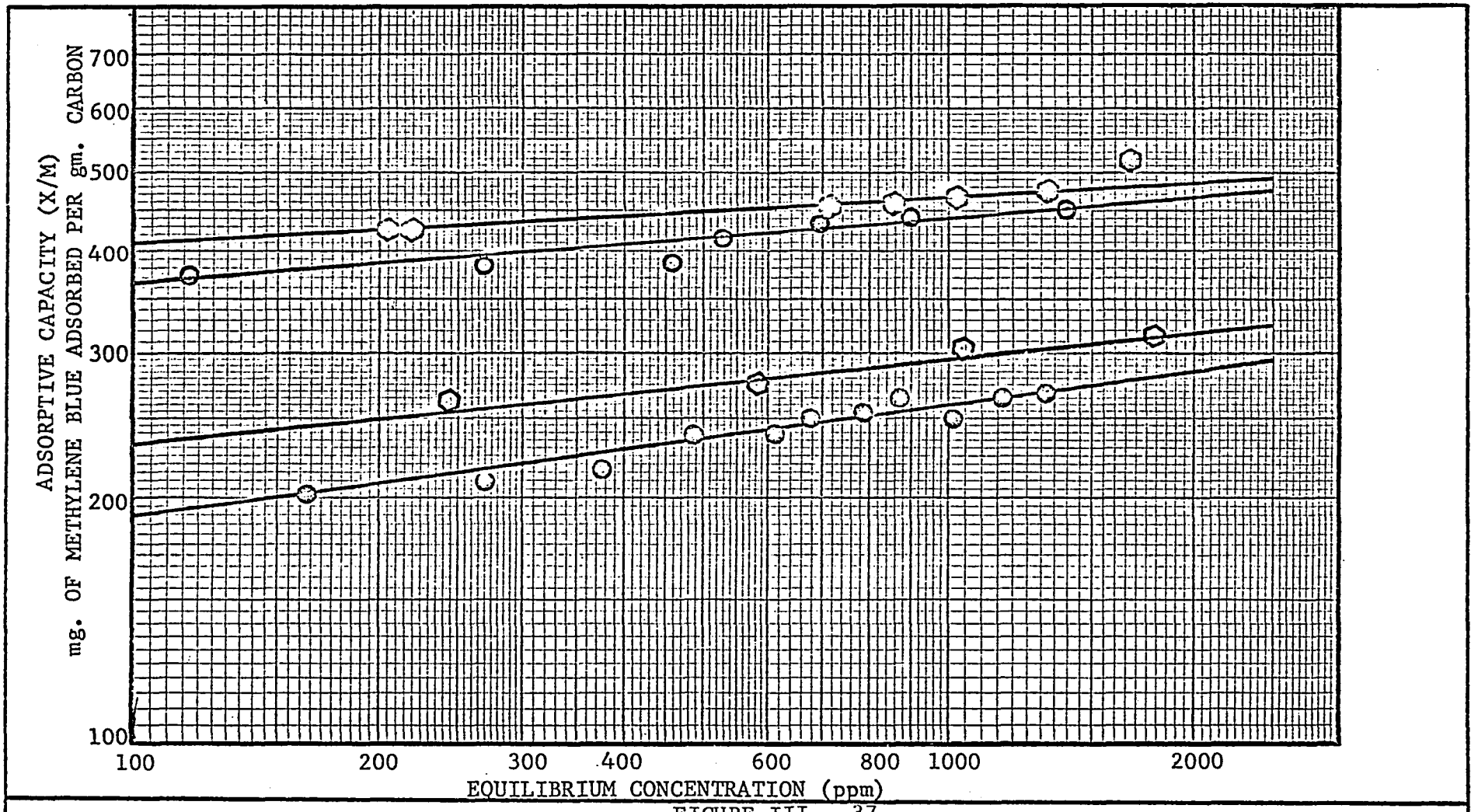

FIGURE III - 37

FREUNDLICH TYPE PLOT OF METHYLENE BLUE ADSORPTION ISOTHERMS FOR ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 9.9% OF THE 2,3 C-C BONDS WERE CLEAVED BEFORE CARBONIZATION

- 79.9% TOTAL BURNOFF
- 80.9% TOTAL BURNOFF
- 83.8% TOTAL BURNOFF
- 86.0% TOTAL BURNOFF

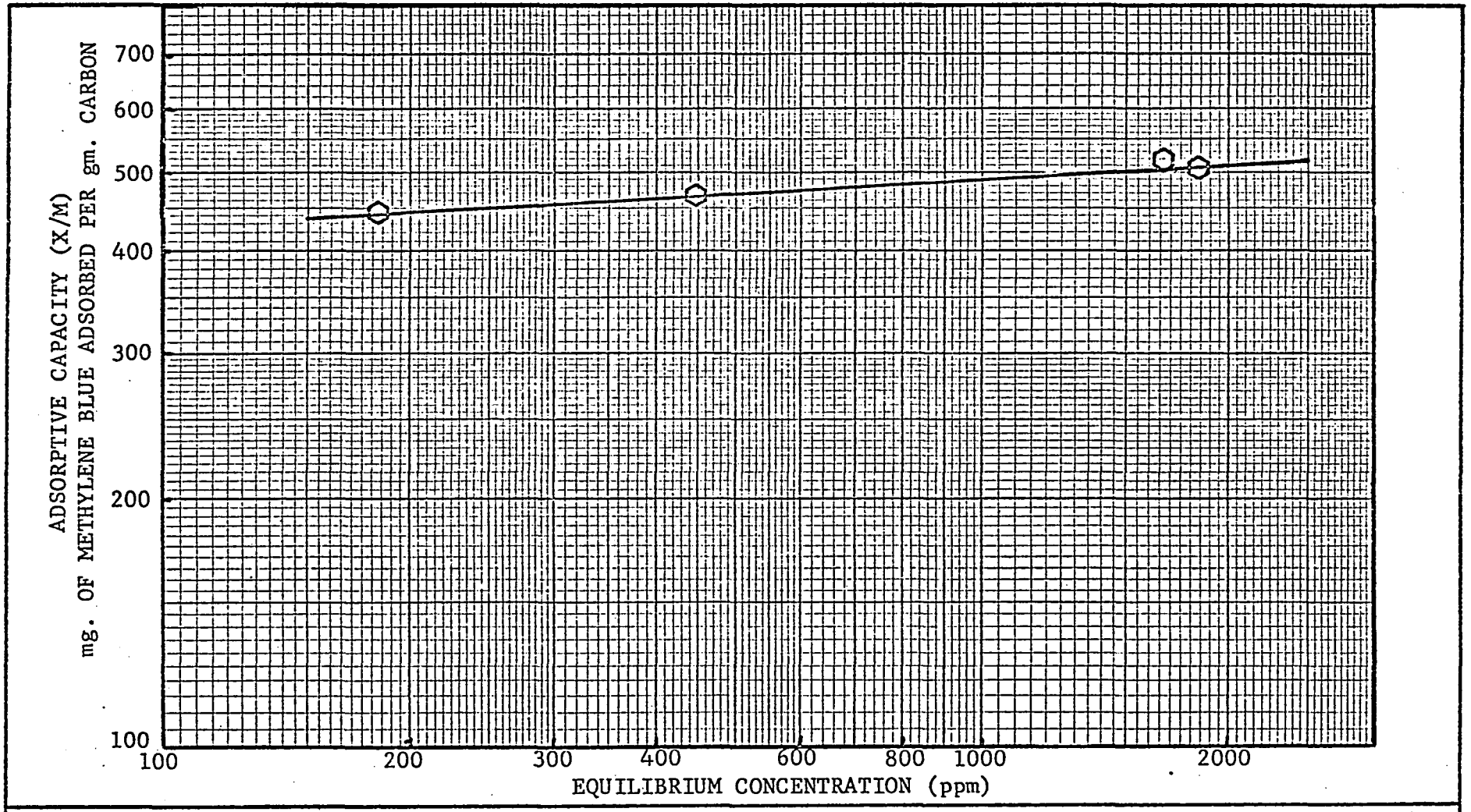

FIGURE III - 38

FREUNDLICH TYPE PLOT OF METHYLENE BLUE ADSORPTION ISOTHERMS FOR ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 16.5% OF THE 2,3 C-C BONDS WERE CLEAVED BEFORE CARBONIZATION

⬡ 88.8% TOTAL BURNOFF

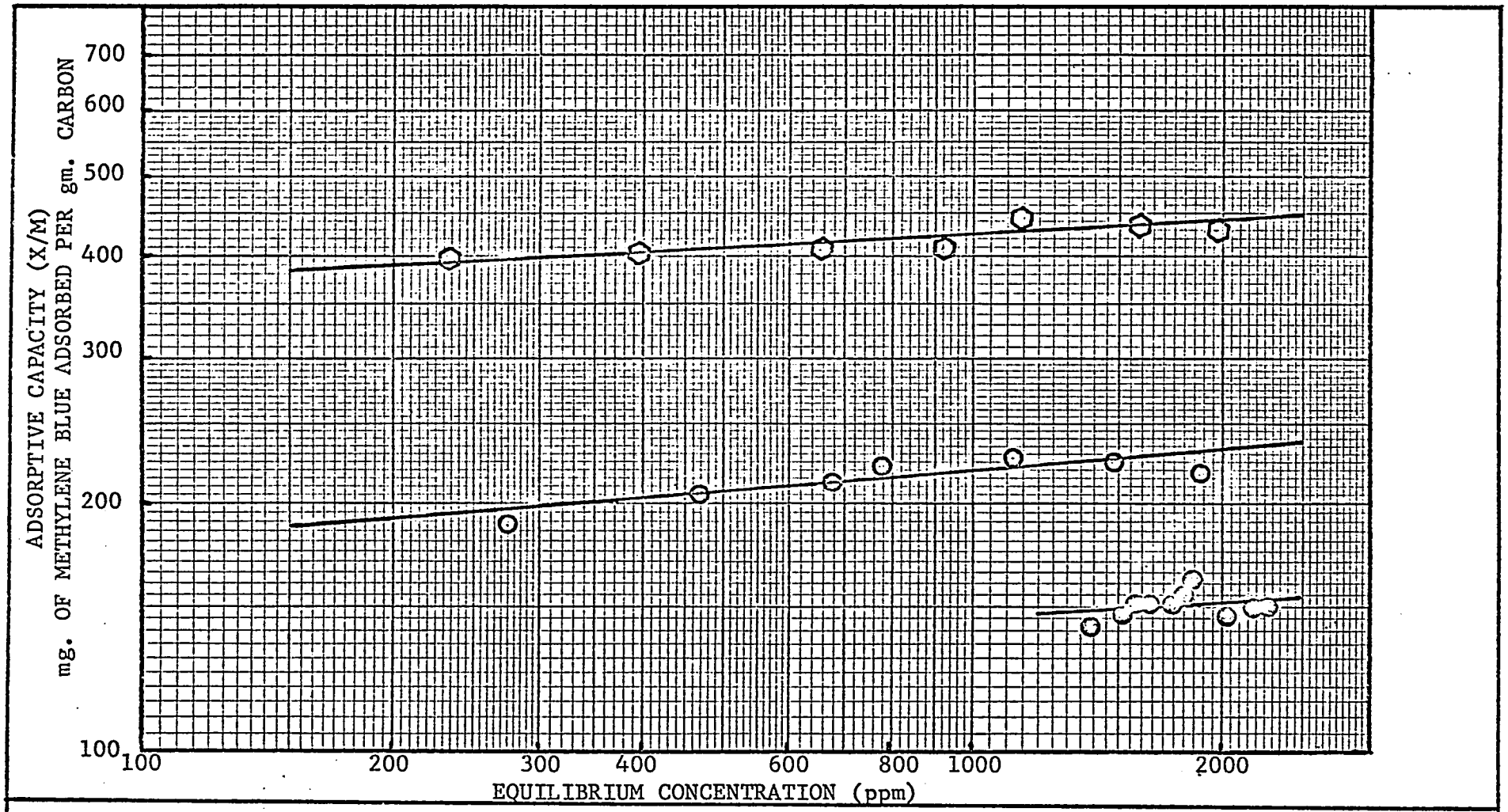

FIGURE III - 39

FREUNDLICH TYPE PLOT OF METHYLENE BLUE ADSORPTION ISOTHERMS FOR ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 19.2% OF THE 2,3 C-C BONDS WERE CLEAVED BEFORE CARBONIZATION

- 76.9% TOTAL BURNOFF
- 77.1% TOTAL BURNOFF
- 82.9% TOTAL BURNOFF

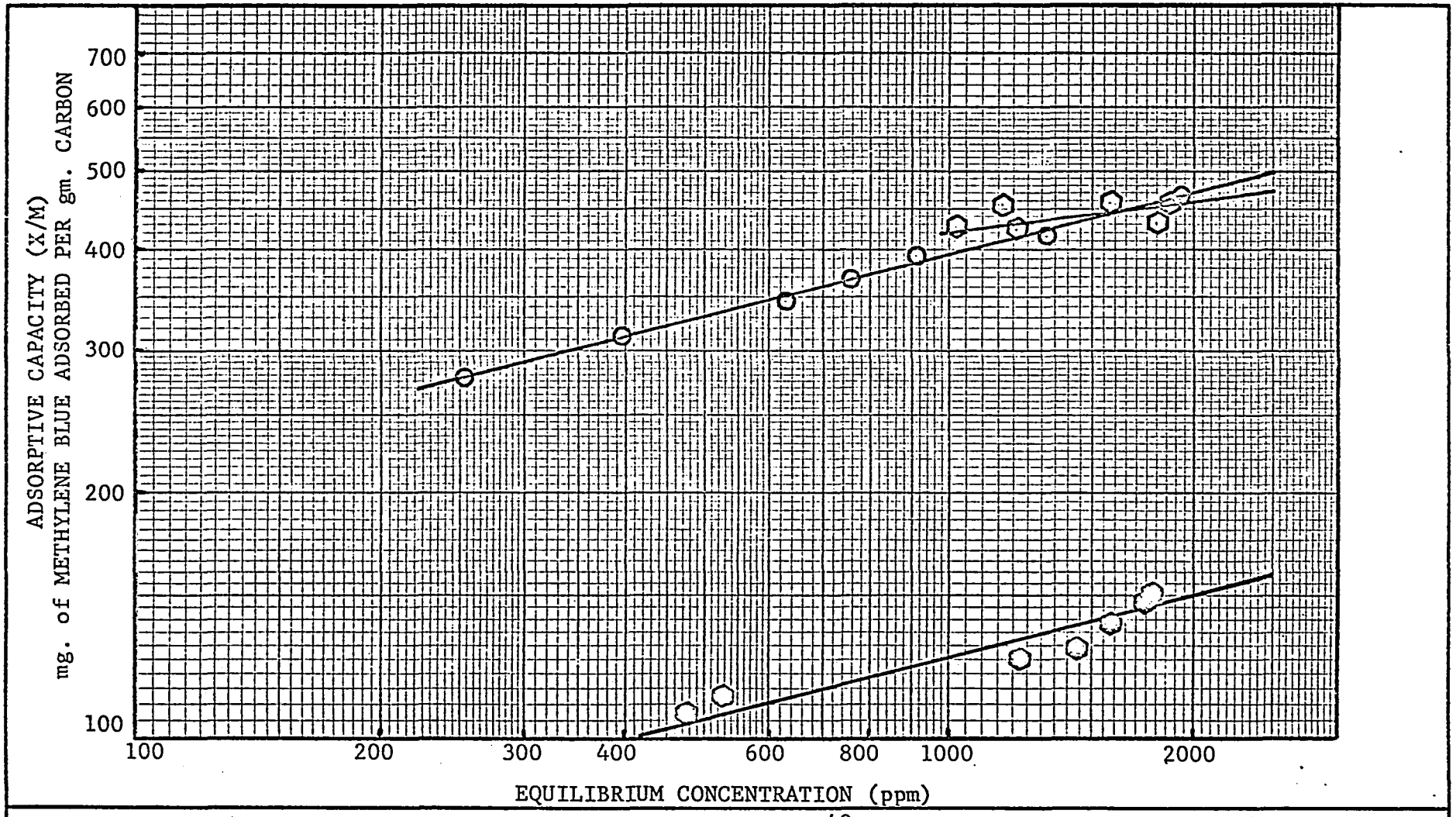

FIGURE III - 40

FREUNDLICH TYPE PLOT OF METHLYENE BLUE ADSORPTION ISOTHERMS FOR ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 29.6% OF THE 2,3 C-C BONDS WERE CLEAVED BEFORE CARBONIZATION

⬡ 77.0% TOTAL BURNOFF

⬡ 82.3% TOTAL BURNOFF

○ 85.2% TOTAL BURNOFF

TABLE III - 6

RELATIVE ADSORPTIVE POWER OF CARBONS PREPARED FROM CELLULOSE IN WHICH THE 2,3 C-C BONDS WERE CLEAVED WITH PERIODIC ACID BEFORE CARBONIZATION.

AMOUNT OF 2,3 C-C BOND CLEAVAGE (%)	TOTAL BURNOFF (%)	ADSORPTIVE CAPACITY AT 2500ppm (2)	RELATIVE ADSORPTIVE CAPACITY
NUCHAR[3] B-100-N	--	270	1.0
0	83.9	300	1.111
0	88.9	320	1.222
0	90.6	285	1.055
<1	90.0	290	1.075
2.3	87.4	348	1.290
2.3	80.3	227	0.841
2.3	79.5	198	0.733
9.9	79.9	295	1.092
9.9	80.9	325	1.203
9.9	83.8	475	1.760
9.9	86.0	490	1.815
16.5	88.8	515	1.910
19.2	76.9	154	0.570
19.2	77.1	237	0.877
19.2	82.9	448	1.662
29.6	77.0	158	0.586
29.6	82.3	470	1.740
29.6	85.2	500	1.853
NUCHAR[4] AQUA A	--	230	0.853

(1) TOTAL BURNOFF IS TOTAL WEIGHT LOSS DURING CARBONIZATION PLUS ACTIVATION.

(2) Mg. METHYLENE BLUE ADSORBED/GRAM OF CARBON.

(3) NUCHAR B-100-N IS A COMMERCIAL ACTIVATED VEGETABLE CHAR THAT WAS USED AS A COMPARATIVE STANDARD.

(4) NUCHAR AQUA A IS ANOTHER COMMERCIAL ACTIVATED VEGETABLE CHAR.

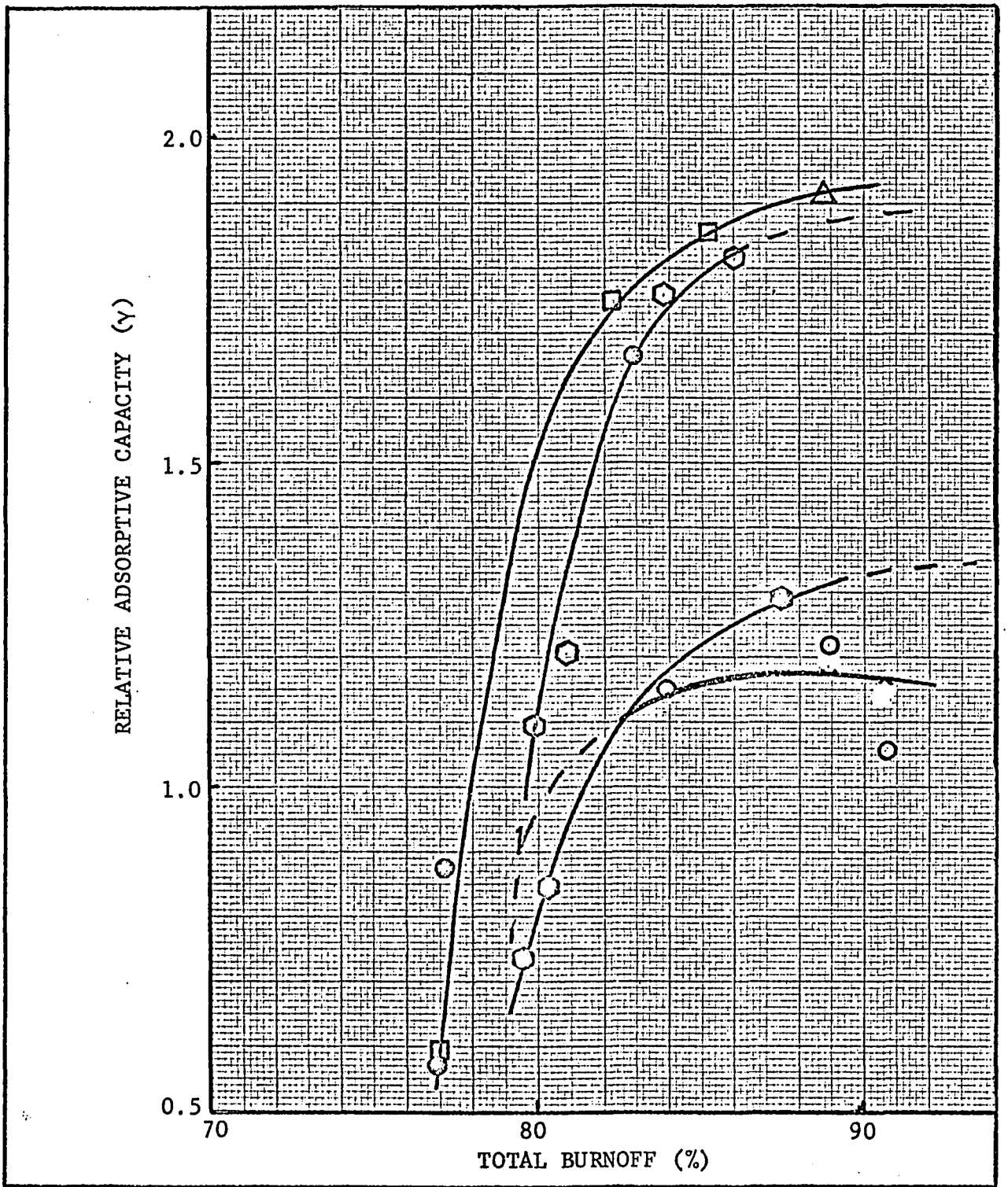

FIGURE III - 41

ADSORPTIVE CAPACITY RELATIVE TO NUCHAR B-100-N FOR THE ADSORPTION OF METHYLENE BLUE AT AN EQUILIBRIUM CONCENTRATION OF 2500ppm ON ACTIVATED CARBON PREPARED FROM CELLULOSE IN WHICH THE 2,3 C-C BONDS WERE CLEAVED WITH PERIODIC ACID BEFORE CARBONIZATION.

- ○ 0% OF 2,3 BONDS CLEAVED
- ⬡ 2.3% OF 2,3 BONDS CLEAVED
- ⬡ 9.9% OF 2,3 BONDS CLEAVED
- △ 16.5% OF 2,3 BONDS CLEAVED
- ⬮ 19.2% OF 2,3 BONDS CLEAVED
- □ 29.6% OF 2,3 BONDS CLEAVED

which 16.5 to 29.6% of the 2,3 C-C bonds had been cleaved. The carbon prepared from cellulose in which 9.9% of the 2,3 C-C bonds were cleaved showed a slightly lower adsorptive capacity than the 16.5 to 29.6% cleavage product but a significantly greater capacity than the 2.3% cleavage products. The 2.3% cleavage product is seen to be slightly better than the uncleaved product. Summarizing these results it appears that the adsorptive capacity increases as the amount of cleavage of the 2,3 C-C bonds is increased up to a value of about 10%. Above 10% cleavage there appears to be very little increase in adsorptive capacity produced by increased cleavage of the 2,3 C-C bonds in the cellulose prior to carbonization.

The carbonized but unactivated material (66-76% burnoff) had adsorptive capacities in the range of 1 to 4 (mg. methylene blue adsorbed/gm. of carbon) at 2500ppm equilibrium concentration. This corresponds to a range of relative adsorptive capacities of 0.004 to 0.015.

Comparison of the results of this study with literature values is difficult since the equilibrium concentration is frequently not included in the published data. Kipling and Wilson (4) report a value of 90 (mg. methylene blue adsorbed/gm. of carbon) for a commerical activated coconut shell carbon at an equilibrium concentration of 2500ppm.

A method of preparing activated carbon which has been widely reported in the recent literature involves treatment of the cellulose with zinc chloride before carbonization. Mukherjee and Bhattacharya (8) report a methylene blue adsorptive capacity of 300-400 (mg. of methylene blue adsorbed/gm. of carbon) for activated carbons made

from ground coconut shell that was mixed with zinc chloride in proportions of 0.9 to 2.7 (gm. of zinc chloride/gm. of coconut shell) before carbonization. Their results may not be directly comparable with the results presented in this study, however, since the concentration of their original methylene blue solution was only 400ppm. The equilibrium concentration was not given in their paper.

Yamada (9) reports a value of about 400(mg. of methylene blue adsorbed/gm. of carbon) at an equilibrium concentration of 2500ppm for activated carbon prepared by mixing equal weights of zinc chloride and filter paper and carbonizing at 900°C for one hour. He refers to a study by Tsuruizumi and Asada (10) and states that they conclude that the optimum condition of activation should occur when "the amount of zinc chloride is double the raw material and the activating temperature is 550°C." It is this reduction of the required activation temperature that makes the zinc chloride treatment so attractive. However, the high corrosive nature of the zinc chloride and the large treatment level required make this process appear unattractive.

The data in this study indicate that activated carbons prepared from cellulose in which some of the 2,3 C-C bonds are cleaved by reaction with periodic acid yields a product that is considerably better than commercial activated carbons when evaluated by the adsorption of methylene blue from water. Also, carbons prepared in this manner appear to be at least as good, if not better, than activated carbons prepared by reaction with zinc chloride before carbonization.

CHAPTER III
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10. Tsuruizumi, A. and Asada, K., J. Chem. Soc. of Japan, Ind. Chem. Sect., 56, 596 (1953).

CONCLUSIONS

1. In batch pyrolysis of bagasse pith the rate at which condensable acid products are formed is enchanced by an acceleration of the heat-up rate and by a decrease in the partial pressure of steam in the reactor. The total amount of acid products formed is relatively unaffected by these variables.

2. The yield of noncondensable gaseous products from the batch pyrolysis of bagasse pith is increased by the addition of steam to the reactor and by an increase in reactor temperature.

3. There is an appreciable difference in the yields and product compositions that are obtained in batch versus continuous pyrolysis of bagasse pith. Therefore, data from batch operations would not be applicable in the design of continuous plants.

4. The noncondensable gases produced by either patch or continuous pyrolysis of bagasse pith are CO, CO_2, H_2, and CH_4. The CH_4 yields at temperatures above 400°C are higher than would be predicted for a Fischer-Tropsch reaction indicating that CH_4 is a primary decomposition product of the bagasse instead of being made in a reforming secondary reaction.

5. The yield of CO, CH_4 and H_2 are increased and the yield of CO_2 is decreased by an increase in reaction temperature.

6. At temperatures above 600°C steam reacts with the carbonatious pyrolysis residue to produce H_2, CO_2 and CO.

7. The gaseous products from the pyrolysis of bagasse pith could be used as a feed to a Fischer-Tropsch synthesis, however, it would

be necessary to increase the hydrogen content. This can be done by either feeding steam to the pyrolysis reactor to increase the hydrogen yield or by feeding a supplemental hydrogen stream to the Fischer-Tropsch reactor.

8. The major liquid organic product from the pyrolysis of bagasse pith is acetic acid which is produced in about 2-4% yield. Other organic products that appear in less than 2% yield include methanol, formaldehyde and formic acid.

9. The continuous pyrolysis of bagasse pith without steam feed shows an increase in gas yield and a decrease in solids residue yield with increasing reactor temperature. The yield of condensable material passes through a maximum between 350 and 500°C.

10. The cleavage of the 2,3 C-C cellulose bonds by periodic acid before pyrolysis proceeds via a reaction which is first order with respect to cellulose and first order with respect to HIO_4. The rate constant for this reaction at 25°C is approximately 2.5×10^{-3} (liters/gm. mol./min.).

11. Cleavage of the 2,3 C-C bonds in the anhydrous glucose units in the cellulose polymer chain by reaction with periodic acid before carbonization and activation produces an increase in the adsorptive capacity of the resulting char. This increase appears to be a result of the increased intramolecular mobility of the polymer chain produced by cleavage of the bond between the vicinal diols in the ring structure. The chars produced by this process are slightly better than those produced by increasing the intermolecular mobility of the cellulose chains by treatment with zinc

chloride before carbonization. The chars produced by either of these processes have about twice the adsorptive capacity that commercially available activated vegetable chars have.

12. The adsorptive capacity of activated carbon prepared from cellulose in which the 2,3 C-C bonds have been cleaved before carbonization increases with increased cleavage up to about 10%. Above 10% there appears to be very little additional increase in the adsorptive capacity produced by further reaction.

13. The results of this study offer confirming evidence for the mechanism of carbonization proposed by Tang and Bacon and for the mechanism of activation proposed by Lamont and Marsh as described in Chapter I.

RECOMMENDATIONS

1. The ability to manufacture better activated carbons from cellulosic materials should grow rapidly in importance as utilization of this material in water purification and industrial waste polution control increases. The high adsorptive capacity of the chars produced by the process developed in this study leads me to recommend that the further development and improvement of this process be continued. Modifications that might yield significant improvements include utilization of other chemicals that will cleave the 2,3 C-C bond in a manner similar to periodic acid (e.g. lead tetraacetate) and chemicals that will cleave the cellulose chain at other locations.

2. In an effort to further utilize cellulosic waste materials, the effect of pressure on the distribution and yield of products should be investigated. Increased pressure should produce an increase in the yield of hydrocarbons. There is a commercial plant currently under construction in Louisiana to produce furfural from bagasse by thermal decomposition at elevated pressures. Results of this study indicate that other commercially attractive products could also be obtained by variation of reactor conditions. It is recommended that this work be done in a continuous rather than a batch reactor.

3. The analysis of the product gas obtained in these studies suggests their potential use as feed material for Fischer-Tropsch synthesis. One advantage that gas produced from pyrolysis of cellulosics should have over that produced from coal is that the pyrolysis gas

would contain no sulfur compounds which will poison the Fischer-Tropsch catalyst. I recommend that additional work in this area be done in a reactor fed continuously from the bottom with the solid residue removed from the top. This would allow the water, which is the first product to be stripped from the decomposing cellulose molecule, to pass over the carbonatious residue as it flows up the reactor. This would yield two desirable results; the hydrogen make would be increased without the necessity of adding steam feed and the steam and carbon dioxide flowing over the carbon dioxide flowing over the carbon would activate this carbon in a one step process. The products from this process would then be an activated carbon and a non-condensable gas stream having an ideal composition to be used as a feed material for a Fischer-Tropsch synthesis.

4. The presence of methanol in the condensed liquid stream suggests the possibility of utilizing a recently reported process for the production of acetic acid*. In this process methanol is reacted with carbon monoxide in the presence of a metal carbonyl catalyst to produce acetic acid.

5. Another interesting research area is the catalytic dealkylation of the lignin present in cellulosics to produce phenol and other products. Since lignin comprises from 10 to 35% of all waste cellulosics investigation of this possibility could produce very rewarding results.

* H. Hohneschutz, N. von Kutepow, and W. Himmele, Hydrocarbon Processing, 45, No. 11, 141-4 (1966).

APPENDIX A

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS OF BAGASSE PITH

TABLE APPENDIX A-1

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITH STEAM FEED

EXPERIMENT 13-10 FEED = 7.7 gm. OF BAGASSE PITH SOLID RESIDUE = (3)

TIME (Min.)	AVG. TEMP. (°C)	STEAM FEED (gm.)	OVERHEAD GAS ($Ft.^3$)	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL%) H_2	CO	CH_4	CO_2
27	370	2.3	0.200	6.7	95.7	0.540	2	28	2	50
44	368	3.7	0.028	4.4	69.1	0.390	3	27	3	48
63	431	4.5	0.019	7.8	124.8	0.704	5	23	5	46
85	406	5.4	0.011	4.7	70.2	0.396	6	22	7	46
105	406	5.1	0.001	4.9	63.3	0.357	7	22	7	44
135	403	6.0	0.001	7.1	79.2	0.446	8	20	8	43
180	409	8.8	0.001	7.8	57.0	0.322	9	19	8	41
240	410	14.0	0	13.5	61.3	0.395	-	-	-	-
305	410	14.4	0	16.7	49.3	0.278	-	-	-	-
329	410	6.3	0	6.6	17.5	0.098	-	-	-	-
362	410	7.6	0	8.0	13.7	0.077	-	-	-	-

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)
(2) EXPRESSED AS GM. OF ACETIC ACID
(3) THE SOLID RESIDUE WAS DISCARDED BEFORE WEIGHING

TABLE APPENDIX A-2

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITH STEAM FEED

EXPERIMENT 13-12 FEED = 90.0 gm. OF BAGASSE PITH SOLID RESIDUE = 33.0

TIME (Min.)	AVG. TEMP. (°C)	STEAM FEED (gm.)	OVERHEAD GAS $_3$ (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
15	280	0.7	0.050	1.8	5.0	0.028	3	32	0	44
20		0.3	0.182	13.0	135.5	0.765	3	29	3	52
27	448	1.6	0.050	7.6	141.0	0.795	8	31	7	43
35		2.2	0.031	5.1	115.9	0.654	15	23	12	39
42	495	2.4	0.019	4.1	97.0	0.547	20	20	12	36
49		2.0	0.018	3.2	67.8	0.383	26	20	13	33
56	530	2.3	0.023	4.1	76.6	0.433	34	17	14	34
63		1.9	0.013	2.4	39.5	0.233	37	15	14	32
70	535	2.6	0.014	3.1	40.0	0.226	40	13	14	32
80		2.2	0.009	3.5	31.0	0.175	42	13	14	32
95	540	4.2	0.013	4.2	30.0	0.169	46	12	14	27
125	549	6.3	0.023	5.5	28.2	0.159	50	9	11	26
155	552	6.4	0.017	7.3	31.3	0.176	54	8	10	26
185	542	6.9	0.013	7.0	15.9	0.090	55	6	9	26
215	540	7.5	0.011	7.5	11.2	0.023	56	8	8	25
245	543	6.7	0.009	7.0	9.5	0.054	57	5	7	25
275	545	8.0	0.006	6.5	7.8	0.044	57	5	7	26
305	542	9.0	0.006	8.9	8.7	0.049	58	5	6	25

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)
(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-3

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITH STEAM FEED

EXPERIMENT 13-14 — FEED = 75.0 gm. OF BAGASSE PITH — SOLID RESIDUE = 24.5 gm.

TIME (Min.)	AVG. TEMP. (°C)	STEAM FEED (gm.)	OVERHEAD GAS $_3$ (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL%) H_2	CO	CH_4	CO_2
15	322	0.2	0.101	2.4	4.5	0.025	3	29	1	59
20		0.3	0.099	7.5	76.0	0.428	-	-	-	-
24	472	0.7	0.038	3.2	59.0	0.333	6	27	6	48
28		1.0	0.017	1.7	30.0	0.169	11	26	9	44
32	515	0.6	0.015	1.5	26.2	0.148	13	24	10	41
37		1.3	0.012	2.1	39.8	0.225	18	26	11	36
45	545	1.4	0.023	3.0	53.4	0.301	27	20	13	33
53		1.6	0.027	2.7	48.0	0.271	36	15	14	27
61	578	2.4	0.023	4.2	74.0	0.417	42	12	15	26
70		3.0	0.025	5.2	37.2	0.210	50	9	12	25
79	610	3.1	0.032	3.9	59.0	0.333	52	8	11	25
92		4.3	0.045	5.1	65.3	0.368	57	6	8	25
100	617	2.5	0.023	3.6	37.3	0.211	59	6	7	25
108		2.6	0.020	2.7	24.6	0.139	56	6	6	25
116	632	1.8	0.022	2.5	19.0	0.107	58	7	5	25
124		2.2	0.031	2.3	15.4	0.087	57	6	5	25
132	664	2.4	0.030	2.7	13.8	0.078	60	6	5	25
140		2.7	0.020	1.8	7.4	0.042	60	6	4	25
150	674	3.0	0.037	2.8	8.5	0.048	60	5	4	25
160		3.0	0.036	2.9	6.3	0.036	60	6	4	25
175	672	4.2	0.049	5.1	6.9	0.039	60	5	3	26
205		6.0	0.061	6.0	10.2	0.058	60	5	3	26
235	676	6.5	0.054	8.4	7.3	0.041	60	5	2	27
265		6.8	0.053	6.3	6.3	0.036	60	5	2	27
300	674	7.5	0.055	6.2	6.0	0.034	60	5	2	27

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)

(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-4

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITH STEAM FEED

EXPERIMENT 13-16 FEED = 69 gm. OF BAGASSE PITH SOLID RESIDUE = 26 gm.

TIME (Min.)	AVG. TEMP. (°C)	STEAM FEED (gm.)	OVERHEAD GAS (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
7	295	4.1	0.100	1.4	9.1	0.051				
11		2.4	0.029	1.9	118.0	0.652	3	32	0	55
16	305	3.1	0.011	3.3	114.4	0.652	3	30	0	57
21		3.2		5.2	88.5	0.498				
26	296	3.2	0.005	4.6	63.4	0.358	2	31	0	57
31		3.0		4.7	49.9	0.282				
36	315	3.8	0.008	4.7	45.3	0.256	2	31	0	57
41		3.3		4.9	49.9	0.282				
46	324	2.6	0.012	4.8	49.7	0.280				
51		2.7		3.8	33.7	0.190				
56	325	2.7	0.009	4.0	27.9	0.157				
61		2.7		3.3	18.7	0.106				
71	322	4.7		5.3	26.6	0.150				
81		3.2	0.009	3.0	14.3	0.081				
91	324	5.4		3.8	16.5	0.093				
101		2.6		4.8	15.2	0.086				
112	329	2.6		2.7	8.6	0.049				
140		8.6		7.7	20.8	0.117				
173	317	9.4		8.8	13.6	0.077				
203		7.2		5.7	6.7	0.038				
233	312	6.7		5.0	4.5	0.025				
263		6.7		6.1	4.1	0.023				
293	315	12.6	0.003	11.3	6.5	0.037				

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)
(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-5

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITHOUT STEAM FEED

EXPERIMENT 13-20 FEED = 86.0 gm. OF BAGASSE PITH SOLID RESIDUE = 41.0 gm.

TIME (Min.)	AVG. TEMP. (°C)	OVERHEAD GAS ($FT.^3$)	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
15	445	0.223	13.2	275.3	1.553	2	33	3	60
25	524	0.087	10.6	124.3	0.686	7	27	14	41
35	507	0.010	1.2	20.0	0.113	9	25	17	36
60	535	0.015	2.2	27.5	0.115	14	23	21	29
85	533	0.009	1.0	10.1	0.057	15	18	21	30
115	536	0.003	0.8	8.0	0.045	16	16	22	30
175	529	0.002	1.0	10.5	0.059	18	16	22	30

THIS REACTION WAS SHUT DOWN BEFORE LIQUID STOPPED COMING OVERHEAD

EXPERIMENT 13-22 FEED = 89.0 gm. OF BAGASSE PITH SOLID RESIDUE = 31.5 gm.

15	316	0.130	5.5	69.6	0.393	2	29	4	61
18	421	0.115	4.3	229.5	1.296	2	31	5	59
21	485	0.040	3.7	90.7	0.511	4	28	12	43
25	556	0.032	1.2	38.5	0.217	11	26	18	35
30	628	0.053	1.2	22.8	0.129	23	18	23	23
40	708	0.045	0.8	13.3	0.075	33	20	21	16
70	753	0.045	4.2	58.3	0.328	36	17	18	15
100	774	0.023	4.6	131.5	0.741	36	18	16	16
110		0.005	0.4	8.0	0.045	36	18	15	16
140	751	0.005	0.4	8.3	0.047	36	20	15	16

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)
(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-6

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITHOUT STEAM FEED

EXPERIMENT 13-24 FEED = 87.0 gm. OF BAGASSE PITH SOLID RESIDUE = 26.0 gm.

TIME (Min.)	AVG. TEMP. (°C)	OVERHEAD GAS $_3$ (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
15	401	0.220	12.8	263.5	1.485	2	31	3	54
17	450	-	5.7	156.3	0.882				
19	495	0.070	2.2	92.7	0.523	5	28	10	43
23	512	0.050	2.3	92.0	0.508	14	22	17	37
28	626	0.040	2.0	58.0	0.327	22	18	21	26
42	698	0.060	2.8	86.2	0.486	29	20	21	20
60	716	0.060	1.8	68.0	0.384	36	19	19	15
90	721	0.024	1.2	34.7	0.196	38	18	17	13
120	723	0.003	2.0	17.0	0.096				
157	725	0	0.5	10.5	0.059				

EXPERIMENT 13-34 FEED = 87.0 gm. OF BAGASSE PITH SOLID RESIDUE = 24.0 gm.

6	158	0.007	1.2	1.5	0.009				
8	242		3.9	16.1	0.091				
10	320	0.008	9.9	300.0	1.690	2	33	1	69
12	380		11.4	340.0	1.920				
14		0.100	4.2	101.0	0.570	2	33	4	52
16	441		2.8	57.4	0.324				
20	473	0.108	2.7	48.6	0.274	2	44	7	40
30	479	0.002	2.8	42.2	0.238	4	30	14	43
60	470	0	0.5	7.0	0.040				
123	483	0	0.8	10.0	0.056				
191	478	0	0.7	7.0	0.040				
270	470	0	0	0	0				

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)
(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-7

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITHOUT STEAM FEED

EXPERIMENT 13-38 FEED = 100.0 gm. OF BAGASSE PITH SOLID RESIDUE 26.9 gm.

TIME (Min.)	AVG. TEMP. (°C)	OVERHEAD GAS $_3$ (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
5	134		2.7	7.9	0.045				
6	207	0.022	2.7	33.5	0.189	3	48	12	29
7			3.2	74.2	0.418				
8	263		4.0	122.2	0.690				
9		0.088	4.4	128.2	0.725	2	36	1	70
9.5			3.1	82.5	0.466				
10	341		2.3	64.3	0.363				
11			3.5	110.0	0.648				
12			3.3	88.0	0.496				
13	370		2.9	72.7	0.411				
14		0.090	1.8	40.8	0.231	1	52	2	44
16			1.4	25.7	0.145				
20	420	0.020	3.2	56.5	0.319	1	36	4	59
25	431	0.002	1.3	22.0	0.124	2	35	7	57
40	458	0.002	0.4	5.1	0.029	2	31	13	50
70	468	0	0.7	11.6	0.066				
132	464		0.3	4.0	0.023				

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)

(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-8

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITHOUT STEAM FEED

EXPERIMENT 13-40 FEED = 92.3 gm. OF BAGASSE PITH SOLID RESIDUE = 18.3 gm.

TIME (Min.)	AVG. TEMP. (°C)	OVERHEAD GAS (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
4	213		8.3	217.3	1.228				
4.5			(*)	228.5	1.290				
5.0			5.2	226.1	1.278	2	38	2	65
5.5	290	0.100	7.2	223.0	1.260				
6.0			3.1	121.4	0.685				
6.5	380		2.5	56.7	0.320				
7			2.0	43.0	0.243				
8			2.0	46.7	0.264				
9	440	0.105	0.8	20.0	0.113	3	37	11	55
13	539	0.033	2.1	39.6	0.223	8	29	22	43
18	582	0.015	1.2	18.0	0.102	15	28	22	32
28	601	0.004	1.6	19.3	0.109	21	20	31	30
48	602	0	0.4	6.2	0.035				
93	590	0	0.2	3.4	0.019				

(*) THIS SAMPLE TITRATED WITHOUT BEING WEIGHED

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)
(2) EXPRESSED AS GM. OF ACETIC ACID

TABLE APPENDIX A-9

ORIGINAL EXPERIMENTAL DATA ON BATCH PYROLYSIS REACTION WITHOUT STEAM FEED

EXPERIMENT 13-44 FEED = 89.2 gm. OF BAGASSE PITH SOLID RESIDUE = 22.0 gm.

TIME (Min.)	AVG. TEMP. (°C)	OVERHEAD GAS $_3$ (FT.^{3})	SAMPLES LIQUID (gm.)	VOL. OF NaOH (1)	TOTAL ACID (2)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
3.5	179		4.7	28.8	0.161				
4.0			2.3	33.7	0.190				
4.5			3.6	72.9	0.411				
5.0			4.4	102.5	0.578				
5.5	331		7.1	187.0	1.055				
6.0			5.0	124.5	0.703				
6.5			3.0	69.6	0.393				
7.0	375		2.0	42.5	0.240				
7.5			0.9	17.2	0.097				
8.0		0.167	1.0	17.0	0.096	2	37	3	61
9.0			1.7	32.5	0.183				
10.5	462	0.018	1.2	21.5	0.121	3	43	5	52
15.0	491		1.8	29.2	0.165				
25	476	0.013	1.5	22.2	0.120	7	30	17	46
60	508	0	0.6	8.0	0.045				

(1) VOLUME OF 0.094 N NaOH USED TO TITRATE OVERHEAD LIQUID (cc.)

(2) EXPRESSED AS GM. OF ACETIC ACID

APPENDIX B

ORIGINAL EXPERIMENTAL DATA ON CONTINUOUS PYROLYSIS OF BAGASSE PITH

TABLE APPENDIX B-1

ORIGINAL DATA FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH

EXPERIMENT 13-54 CHARGE TO FEED RESERVOIR = 175 gm.
SOLID RESIDUE = 35.0 gm. PITH NOT FED = 102.0 gm.

TIME (MIN.)	AVG. TEMP. (°C)	OVERHEAD LIQUID AMOUNT (GM.)	OVERHEAD LIQUID ACETIC ACID**	GAS ($FT.^3$)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
5	326	0		0				
10	325	0		0.002				
15	323	0		0.001				
20	338	0		0.002	1	45	2	39
25	327	0		0.004	2	43	2	38
30	329	0		0.005	2	42	2	39
35	330	0.5	7.3	0.006	1	43	2	39
40	333	0.7	7.7	0.010	2	48	1	38
45	335	0.9		0.009	1	53	1	35
50	333	0.8	7.1	0.007	1	58	1	32
55	337	0.7	6.8	0.006				
60	335	0.5		0.005	1	62	1	29
70	334	0.9		0.009	1	62	1	29
80	336	1.5		0.013	1	60	1	29
90	332	1.1	7.0	0.010	1	56	1	32
105	323	1.3		0.011	2	49	1	37
120	324	1.1		0.010	2	43	1	39
135	327	1.9		0.019	2	33	1	50
150	324	0.7		0.020	2	26	1	54
165	335	0.4		0.020	3	28	1	59
180	331	1.5		0.014	3	28	1	62
195	334	2.3		0.019	3	29	1	62
210*	335	1.6		0.012	3	29	1	64
228	321	1.1		0.002	3	28	1	64

* LEVEL IN FEED RESERVOIR NOT GOING DOWN

** WT. % AS MEASURED BY GAS CHROMATOGRAPHY

TABLE APPENDIX B-2

ORIGINAL DATA FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH

EXPERIMENT 13-56
SOLID RESIDUE = 35.0 gm.

CHARGE TO FEED RESERVOIR = 100.7 gm.
PITH NOT FED = 37.0 gm.

TIME (MIN.)	AVG. TEMP. (°C)	OVERHEAD LIQUID AMOUNT (GM.)	OVERHEAD LIQUID ACETIC ACID**	GAS (FT^3)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
10	435	0.2		0.006	2	31	1	56
15	435	0.8	7.5	0.008	2	31	1	56
20	439	0.6		0.008	2	30	1	56
30	445	0.7	7.4	0.016	2	27	1	59
40	443	0.7	7.1	0.024	3	28	1	56
60	443	0.7	6.8	0.035	3	30	2	56
90	425	1.0	10.5	0.040	4	32	2	56
125	440		8.8	0.059	4	33	3	54
163	427	1.6	9.8	0.035				
187	433	*		0				
204	438			0				

* LIQUID OVERHEAD SAMPLING VALVE FOUND TO BE PLUGGED. TOTAL SAMPLE REMOVED AT END OF RUN = 14 gm.

** WT. % AS MEASURED BY GAS CHROMATOGRAPHY.

TABLE APPENDIX B-3

ORIGINAL DATA FOR CONTINUOUS PYROLYSIS OF BAGASSE PITH

EXPERIMENT 13-60 — CHARGE TO FEED RESERVOIR = 98.0 gm.
SOLID RESIDUE = 27.2 gm. — PITH NOT FED = 11.0 gm.

TIME (MIN.)	AVG. TEMP. (°C)	OVERHEAD LIQUID AMOUNT (GM.)	OVERHEAD LIQUID ACETIC ACID**	GAS ($FT.^3$)	GAS COMPOSITION (MOL %) H_2	CO	CH_4	CO_2
10	512	0.1		0.015				
20	512	2.0	7.8	0.040				
30	507	2.0		0.050	3	34	5	28
40	508	2.2	10.2	0.043	4	36	7	33
60	503	3.8	10.7	0.077	5	39	10	35
90	509	4.6	9.3	0.117	5	39	10	37
120	507	4.8	10.9	0.112	5	40	10	37
141	507	1.9	12.5	0.029	5	40	10	35
150	507	0.4		0				

5 gm. OF LIQUID WAS COLLECTED THROUGHOUT THIS RUN IN A SECOND RECEIVER THAT WAS IMMERSED IN AN ICE-WATER BATH.

EXPERIMENT 13-62 — CHARGE TO FEED RESERVOIR = 100.0 gm.
SOLID RESIDUE = 26.6 gm. — PITH NOT FED = 2.0 gm.

4	627			0.017				
8	631	0.1		0.038				
12	628			0.038				
20	635	0.2		0.072	7	45	15	22
30	634	4.3	4.3	0.084	5	38	14	16
45	626	1.9	5.1	0.154	7	43	15	18
60	621	2.1		0.167	7	45	15	20
75	620	2.5		0.171	7	45	15	20
90	626	2.5		0.168	7	45	15	20
105	625	3.0		0.145	7	46	15	20
115	FEED RESERVOIR EMPTY							
120	634	4.4		0.096	7	45	14	20
135	637	1.7		0.003				
151		0.8		0.002				

** WT. % AS MEASURED BY GAS CHROMATOGRAPHY.

APPENDIX C

ORIGINAL EXPERIMENTAL DATA FOR HIO_4 CLEAVAGE REACTION

TABLE APPENDIX C-1

ORIGINAL EXPERIMENTAL DATA FOR HIO_4 CLEAVAGE REACTION

EXPERIMENT 13-99
CELLULOSE FED = 310.3 gm. FINAL CLEAVAGE = 29.6%
HIO_4 FED = 1.98 LITERS OF 0.5385 M SOLUTION

TIME (MIN.)	C_A(1)	C_B(2)	C_B/C_A
0	0.5385	0.960	1.770
11	0.526	0.950	1.805
21	0.513	0.940	1.833
50	0.462	0.885	1.915
75	0.460	0.883	1.918
126	0.415	0.844	2.03
177	0.392	0.818	2.09
213	0.340	0.718	2.11
357	0.279	0.703	2.52
385	0.280	0.704	2.51
400	0.253*	0.676	2.67

EXPERIMENT 13-105
CELLULOSE FED = 208.5 gm. FINAL CLEAVAGE = 19.6%
HIO_4 FED = 2.40 LITERS OF 0.5850 M SOLUTION

0	0.585	0.536	0.917
20	0.518	0.469	0.905
40	0.585	0.536	0.917
60	0.552	0.503	0.912
120	0.521	0.472	0.905
190	0.501	0.452	0.901
240	0.464	0.415	0.896
250	0.482*	0.433	0.899

* ANALYSIS OF FILTRATE FROM FINAL REACTION MIXTURE

(1) CONCENTRATION OF HIO_4 (MOLS/LITER)

(2) CONCENTRATION OF UNREACTED CELLULOSE (MOLS/LITER)

TABLE APPENDIX C-2

ORIGINAL EXPERIMENTAL DATA FOR HIO_4 CLEAVAGE REACTION

EXPERIMENT 7-58
CELLULOSE FED = 179.5 gm. FINAL CLEAVAGE = 2.3%
HIO_4 FED = 2.50 LITERS OF 0.1301 M SOLUTION

TIME (MIN.)	C_A(1)	C_B(2)	C_B/C_A
0	0.1301	0.443	3.41
7	0.1285	0.442	3.44
13	0.1285	0.442	3.44
15	0.1280	0.441	3.45
26	0.1275	0.441	3.45
30	0.1259	0.439	3.49
35	0.1227	0.436	3.55
40	0.1217	0.435	3.57
45	0.1198*	0.433	3.61

EXPERIMENT 13-107
CELLULOSE FED = 277.3 gm. FINAL CLEAVAGE = 9.9%
HIO_4 FED = 2.775 LITERS OF 0.500 M SOLUTION

0	0.500	0.617	1.234
10	0.443	0.560	1.264
28	0.486	0.603	1.241
30	0.478	0.594	1.243
51	0.450	0.567	1.260
62	0.439*	0.556	1.267

EXPERIMENT 7-53
CELLULOSE FED = 91 gm. FINAL CLEAVAGE = 16.5%
HIO_4 FED = 1.78 LITERS OF 0.466 M SOLUTION

0	0.466	0.315	0.676
20	0.436	0.285	0.653
30	0.421	0.270	0.641
42	0.414*	0.263	0.636

* ANALYSIS OF FILTRATE FROM FINAL REACTION MIXTURE
(1) CONCENTRATION OF HIO_4 (MOLS/LITER)
(2) CONCENTRATION OF UNREACTED CELLULOSE (MOLS/LITER)

APPENDIX D

ORIGINAL EXPERIMENTAL DATA ON ADSORPTION OF METHYLENE BLUE BY ACTIVATED CARBON

TABLE APPENDIX D-1

ORIGINAL EXPERIMENTAL DATA FOR ADSORPTION OF METHYLENE BLUE FROM WATER USING ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 0% OF THE 2,3 C-C BONDS WERE CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION. EACH SAMPLE CONTAINED 35 cc. OF SOLUTION HAVING AN ORIGINAL METHYLENE BLUE CONCENTRATION OF 2480 ppm.

EXPERIMENT 13-100 TOTAL BURNOFF = 83.9%			EXPERIMENT 13-106 TOTAL BURNOFF = 88.9%			EXPERIMENT 13-115 TOTAL BURNOFF = 90.6%		
CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.3116	767	193	0.3052	726	201	0.2859	898	194
0.2529	908	217	0.2416	898	230	0.2458	1010	210
0.2020	1110	237	0.1954	1110	245	0.2050	1202	211
0.1855	1212	239	0.1737	1212	255	0.1809	1303	228
0.1565	1363	250	0.1575	1293	264	0.1533	1413	244
0.1035	1716	258	0.1235	1545	265	0.1190	1635	248
0.0764	1889	271	0.0790	1870	270	0.0952	1798	250
0.0429	2120	294	0.0404	2130	304			

(1) mg. OF METHYLENE BLUE ADSORBED/gm. OF CARBON

TABLE APPENDIX D-2

ORIGINAL EXPERIMENTAL DATA FOR ADSORPTION OF METHYLENE BLUE FROM WATER USING ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 2.3% OF THE 2,3 C-C BONDS WERE CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION. EACH SAMPLE CONTAINED 35 cc. OF SOLUTION HAVING AN ORIGINAL METHYLENE BLUE CONCENTRATION OF 2480 ppm.

EXPERIMENT 7-62 TOTAL BURNOFF = 79.5%			EXPERIMENT 7-63 TOTAL BURNOFF = 80.3%			EXPERIMENT 7-60 TOTAL BURNOFF = 87.4%		
CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.2901	929	183	0.3135	889	178	0.3108	253	239
0.2478	1162	186	0.2447	1172	187	0.2476	535	275
0.2023	1464	176	0.1928	1464	184	0.1894	858	300
0.1817	1545	180	0.1556	1566	205	0.1776	959	299
0.1502	1737	173	0.1198	1768	208	0.1435	1212	309
0.1106	1919	177	0.0794	2040	194	0.1096	1464	325
0.0797	2070	180	0.0391	2192	257	0.0823	1717	325
0.0449	2222	201	0.3082	869	183	0.0472	2050	318
0.3024	869	186	0.2384	1182	190	0.2912	293	262
0.2819	1050	178	0.1915	1374	202	0.2323	626	279
0.2014	1414	183	0.0552	2070	259	0.1965	859	288
0.1915	1525	175				0.1876	909	293
0.1509	1737	175				0.1445	1212	307
0.1107	1969	161				0.1157	1464	308
0.0790	2070	181						
0.0473	2222	191						

(1) mg. OF METHYLENE BLUE ADSORBED/gm. OF CARBON

TABLE APPENDIX D-3

ORIGINAL EXPERIMENTAL DATA FOR ADSORPTION OF METHYLENE BLUE FROM WATER USING ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 9.9% OF THE 2,3 C-C BONDS WERE CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION. EACH SAMPLE CONTAINED 35 cc. OF SOLUTION HAVING AN ORIGINAL METHYLENE BLUE CONCENTRATION OF 2480 ppm.

EXPERIMENT 13-110
TOTAL BURNOFF = 79.9%

CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.4499	61	192
0.4124	163	201
0.3798	269	209
0.3510	374	216
0.2998	485	239
0.2807	603	240
0.2599	673	250
0.2403	783	255
0.2206	865	265
0.1997	1005	250
0.1802	1165	265
0.1600	1305	268

EXPERIMENT 13-106
TOTAL BURNOFF = 80.9%

CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.6775	1.1	131
0.3080	242	262
0.2505	580	275
0.0846	1780	316
0.1725	1045	304

EXPERIMENT 13-118
TOTAL BURNOFF = 86.0%

CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.2366	3.5	377
0.1921	204	427
0.1899	217	428
0.1417	712	453
0.1298	848	457
0.1147	1010	467
0.0909	1312	475
0.0591	1665	520

EXPERIMENT 13-116
TOTAL BURNOFF = 83.8%

CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.2503	27.4	354
0.2300	116	371
0.2102	267	381
0.1904	455	386
0.1704	525	416
0.1501	697	432
0.1305	899	442
0.0907	1385	450

(1) mg. OF METHYLENE BLUE ADSORBED/gm. OF CARBON

TABLE APPENDIX D-4

ORIGINAL EXPERIMENTAL DATA FOR ADSORPTION OF METHYLENE BLUE FROM WATER USING ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 19.2% OF THE 2,3 C-C BONDS WERE CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION. EACH SAMPLE CONTAINED 35 cc. OF SOLUTION HAVING AN ORIGINAL METHYLENE BLUE CONCENTRATION OF 2480 ppm.

EXPERIMENT 13-109 TOTAL BURNOFF = 76.9%			EXPERIMENT 13-111 TOTAL BURNOFF = 77.1%			EXPERIMENT 13-113 TOTAL BURNOFF = 82.9%		
CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.2991	1385	142	0.4108	273	188	0.1121	1142	446
0.2794	1508	149	0.3514	465	201	0.0488	1945	430
0.2599	1515	146	0.3051	636	212	0.2040	232	397
0.2407	1568	151	0.2695	768	222	0.1830	394	401
0.2200	1648	151	0.2090	1120	228	0.1575	656	407
0.2011	1728	151	0.1562	1475	225	0.1341	919	409
0.1820	1788	155	0.0985	1870	217	0.0795	1585	437
0.1606	1865	162						
0.1396	2010	146						
0.1203	2030	164						
0.1000	2170	149						
0.0806	2250	150						

(1) mg. OF METHYLENE BLUE ADSORBED/gm. OF CARBON

TABLE APPENDIX D-5

ORIGINAL EXPERIMENTAL DATA FOR ADSORPTION OF METHYLENE BLUE FROM WATER USING ACTIVATED CARBON MADE FROM CELLULOSE IN WHICH 29.6% OF THE 2,3 C-C BONDS WERE CLEAVED BY REACTION WITH PERIODIC ACID BEFORE CARBONIZATION. EACH SAMPLE CONTAINED 35 cc. OF SOLUTION HAVING AN ORGINAL METHYLENE BLUE CONCENTRATION OF 2480 ppm.

EXPERIMENT 13-101 TOTAL BURNOFF = 77.0%			EXPERIMENT 13-104 TOTAL BURNOFF = 82.3%			EXPERIMENT 13-108 TOTAL BURNOFF = 82.9%		
CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.3108	1434	129	0.2976	36.4	341	0.2927	252	279
0.2528	1585	138	0.1522	1012	429	0.2461	394	311
0.2008	1738	147	0.1206	1205	423	0.1980	626	346
0.1905	1758	151	0.1229	1152	455	0.1729	758	369
			0.0801	1588	455	0.1494	909	392
			0.0710	1748	430	0.1066	1313	417
			0.0571	1830	453	0.0473	1949	468

(1) gm. OF METHYLENE BLUE ADSORBED/gm. OF CARBON

TABLE APPENDIX D-6

ORIGINAL EXPERIMENTAL DATA FOR ADSORPTION OF METHYLENE BLUE FROM WATER USING COMMERCIAL ACTIVATED CARBON

EXPERIMENT 7-50 NUCHAR AQUA A			EXPERIMENT 7-61 NUCHAR B-100-N		
CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)	CARBON (gm.)	EQUILIBRIUM CONCENTRATION (ppm.)	X/M (1)
0.1966	1255	230	0.2503	677	252
0.1698	1432	230	0.2126	909	258
0.1485	1545	236	0.1981	1010	260
0.1162	1775	232	0.1542	1364	253
0.1009	1900	224	0.1466	1374	264
0.0783	2130	186	0.1136	1616	266
0.0487	2225	230	0.0871	1838	258
0	2545	-	0.0410	2121	265

(1) mg. OF METHYLENE BLUE ADSORBED/gm. OF CARBON

VITA

Walter R. Williamson was born in Quitman, Mississippi on October 28, 1938. He lived in various locations throughout the South before being graduated from Aiken High School in Aiken, South Carolina in June 1956. He then attended the University of Delaware from which he received a Bachelor of Science Degree in Chemical Engineering in June 1961. After graduation he worked for Hercules Powder Company for three years doing research and plant technical work.

In December, 1963 he married the former Miss Susan Stewart of Wilmington, Delaware. In September, 1964 he enrolled at Louisiana State University to pursue a Ph.D. Degree in Chemical Engineering. Following completion of this work, he will assume a position in the Research Division of the Plastics Department of E. I. duPont de Nemours and Co. in Wilmington, Delaware.

EXAMINATION AND THESIS REPORT

Candidate: Walter Randall Williamson

Major Field: Chemical Engineering

Title of Thesis: Activated Carbon and Pyrolytic Decomposition Products from Cellulosics

Approved:

J. Clayton D. Callihan
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination:

November 10, 1967